OF 2002-2

Open File

New Nouveau
Brunswick

Natural Resources and Energy
Minerals, Policy and Planning

# NEW PROCESS FOR INDUSTRIAL MINERALS

W.J. Wilson and Associates Ltd.

ISSN 1702-2649
ISBN 1-55236-777-0
Price: $12.00

2002

Open File 2002-2

New Process for Industrial Minerals

Recommended citation:

W.J. WILSON AND ASSOCIATES LTD. 2002. New process for industrial minerals. New Brunswick Department of Natural Resources and Energy, Minerals, Policy and Planning Division, Open File 2002-2, 75 p.

---

Prepared for:

**Minerals, Policy and Planning Division**
Department of Natural Resources and Energy
Province of New Brunswick

**Hon. Jeannot Volpé**
Minister of Natural Resources and Energy

April, 2002

New Nouveau
Brunswick

Natural Resources and Energy
Minerals, Policy and Planning

**Open File 2002-2**

# NEW PROCESS FOR INDUSTRIAL MINERALS

W.J. Wilson and Associates Ltd.

*This report has been prepared by W.J. Wilson and Associates Ltd., Saint John, New Brunswick for the Province of New Brunswick. The document has been published as received from the author.*
*Value-added/Mineral Processing Program report received April, 2000.*

---

*Le présent rapport a été préparé par W.J. Wilson and Associates Ltd., de Saint John, en Nouveau-Brunswick à l'intention de la province du Nouveau-Brunswick. Le document a été publié sous la forme où il a été reçu de l'auteur.*
*Rapport du Programme de traitement des minéraux à valeur ajoutée reçu en avril 2000.*

ISSN 1702-2649
ISBN 1-55236-777-0
Price: $12.00

2002

**W.J. Wilson and Associates Ltd.**
Industrial/Chemical Consultants
55 Smythe St., Apt. 514
Saint John, NB
E2L 5A2

Fax: 1 (506) 468-2575
Res: 1 (506) 657-7185

March 9, 2000

# NEW PROCESS FOR INDUSTRIAL MINERALS

Final Report for File No: 566-06-0003

W.J. Wilson and Associates Ltd.
W.J. Wilson, President

## ABSTRACT

Previous work had been done with the Higgins Loop where we got 8% caustic soda and fixed bed studies where we achieved 11.5% NaOH. In both cases a dilute calcium chloride solution was the waste product. Tetra Technologies informed us that they had successfully processed up to 8% slurries of suitable size in their system, and gave us what turned out to be a computer simulation of our process giving in excess of 10% caustic and 6 to 7% calcium chloride. So we made the decision to try this system. The report on this study is attached to this report as Appendix 1. The results obtained gave only 4% NaOH and 1% calcium chloride. A very unsatisfactory result, and our efforts to have them modify the system in the light of our fixed bed studies were unsuccessful. We therefore abandoned further work on the Higgins Loop system and terminated the work at their pilot plant.

We researched the reason for the inadequate exchange of the 4% slurry and extended this to 2%, 0.5%, and 0.1% slurries. This showed that the exchange was dependant on two factors. The time involved in the exchange, the longer the time the more effective the exchange, and concurrently the more dilute the slurry the better the exchange. These results are given in Appendix 2.

We then studied how to incorporate these findings in a system which would give 10+% caustic soda, or the equivalent in caustic potash, as well as 6 to 7% calcium chloride in the effluent. Appendix 3.

Appendix 4 was successful in demonstrating how this might be done and we concluded that such a process was feasible in a fixed bed system, and possibly in a Higgins Loop, so that these objectives can be reached. Included in this is the treatment of lime in a static mode where the lime is added to the bed and then is allowed to sit in contact with the resin for 1 to 2 hours. This has enabled us to project what the ultimate system would be like and it is as follows.

1. Pass in the lime slurry to the column and allow to stand for 1 to 2 hours until equilibrium is achieved.
2. Wash the residual lime and the chloride released from the resin out for later workup to give the calcium chloride byproduct.
3. Treat the column with the tails from the previous cycle to further strip the resin of chloride.
4. Treat the resin with potassium chloride, made up in the solution from #3, to generate appropriate levels of caustic and return the resin to the chloride form.

We are now going to, in future work, fine tune the cycle and prepare material balances etc. preparatory to engineering a full scale system. This will not be part of the VAMP work.
We have also started studies on how to apply this technology to the carbonate cycle.

RÉSUMÉ

Nous avions obtenu 8 % d'hydroxyde de sodium au cours de travaux antérieurs réalisés au moyen de la boucle Higgins et 11,5 % de NaOH lors d'études à l'aide de lits fixes. Dans les deux cas, le déchet produit a été une solution diluée de chlorure de calcium. La Tetra Technologies nous a avisés qu'elle avait réussi à traiter jusqu'à 8 % de boues liquides de taille convenable par sa méthode et elle nous a fourni ce qui s'est avéré une simulation par ordinateur de notre procédé produisant plus de 10 % d'hydroxyde de sodium et de 6 à 7 % de chlorure de calcium. Nous avons donc pris la décision de faire l'essai de cette méthode. Le compte rendu de cette étude est annexé au présent rapport à l'annexe 1. Les résultats obtenus ont seulement donné 4 % de NaOH et 1 % de chlorure de calcium. Ces résultats étaient très insatisfaisants et nos efforts en vue d'amener la TT à modifier la méthode employée à la lumière des études que nous avons menées à l'aide de lits fixes, ont été vains. Nous avons par conséquent abandonné les travaux par la méthode à boucle Higgins et mis fin aux travaux en cours à l'installation pilote de la société.

Nous avons cherché à découvrir la raison de l'échange inadéquat des 4 % de boue liquide et nous avons élargi cette étude à des taux de 2 %, 0,5 % et 0,1 % de boue liquide. Ces recherches nous ont révélé que l'échange est tributaire de deux facteurs : la durée de l'échange plus l'échange dure longtemps, plus il est efficace et, simultanément, plus les boues liquides sont diluées, meilleur est l'échange. L'annexe 2 fait état de ces résultats.

Nous avons ensuite étudié de quelle façon nous pourrions incorporer ces constatations dans une méthode qui fournirait plus de 10 % d'hydroxyde de sodium ou l'équivalent en hydroxyde de potassium ainsi que de 6 à 7 % de chlorure de calcium dans l'effluent. Annexe 3.

L'annexe 4 a réussi à démontrer de quelle façon on pouvait y parvenir et nous en avons conclu qu'il était possible de recourir à une telle méthode dans un procédé à lit fixe, et possiblement un procédé à boucle Higgins, pour atteindre ces objectifs. Le procédé englobe le traitement de la chaux en mode statique avec l'addition de chaux au lit et son maintien au repos en contact avec la résine pendant une à deux heures. Cette façon de faire nous a permis de prévoir le mode de fonctionnement du procédé ultime, qui se déroulerait comme suit.

1. Faire circuler la boue liquide de chaux dans la colonne et la laisser reposer pendant une à deux heures jusqu'à l'obtention d'un équilibre.
2. Éliminer la chaux résiduelle et le chlorure s'étant libéré de la résine aux fins du traitement ultérieur qui fournira le chlorure de calcium secondaire.
3. Traiter la colonne au moyen des produits de queue du cycle précédent pour enlever davantage de chlorure de la résine.

4. Traiter la résine à l'aide de chlorure de potassium, obtenu dans la solution provenant de la troisième étape, pour produire les niveaux voulus d'hydroxyde de potassium et ramener la résine sous forme de chlorure.

Au cours de nos travaux futurs, nous ferons une mise au point finale du cycle et préparerons es bilans matières et les autres documents préparatoires à la mise au point technique d'un système à grande échelle. Ces travaux ne feront pas partie des travaux réalisés en vertu du PTMVA. Nous avons également commencé des études sur la façon d'appliquer ces techniques au cycle des carbonates.

## Table of Contents

New Process For Industrial Minerals
Final Report for VAMP Project No. 566-06-0003


| | | |
|---|---|---|
| 1. | Abstract | |
| 2. | List of Figures and List of Tables. | 1 |
| 3. | Acknowledgements | 2 |
| 4. | Introduction - Objective | 3 |
| | - Scope | 3 |
| | - Background | 3 |
| 5. | Project Methodology | 4 |
| 6. | Results and Discussions | 5 |
| 7. | Conclusions and Recommendations | 5 |
| 8. | References | 6 |
| 9. | Appendices | 7 |

Appendix 1 Higgins Loop Pilot Test Report ——— 9

| | | |
|---|---|---|
| A. | Executive Summary | 1 |
| B. | Background | 4 |
| C. | Process Description | 6 |
| D. | Test Program Description | 8 |
| E. | Conclusions and Recommendations | 14 |
| F. | Appendices | 17 |
| | Resin Technical Data | |
| | Individual Test Reports | |
| | Project Economics | |

Appendix 2

The Manufacture of Caustic Alkali from Lime and Salt by Ion Exchange. Studies with Tetra Technologies Pilot Plant in Clinton, Tennessee. ——— 39

| | | |
|---|---|---|
| 1. | Abstract | |
| 2. | List of Figures and Acknowledgements | 1 |
| 3. | Introduction | 2 |
| 4. | Point by Point Discussion of Report | 4 |
| 5. | Test Program Discussions | 7 |
| 6. | Conclusions | 8 |
| 7. | References and Appendices | 10 |

TABLE OF CONTENTS con't.

Appendix 3

Development of a Caustic Process Using Fixed Bed Ion Exchanging. 53

1. Abstract
2. Introduction 1
3. Objectives 1
4. Experimental 2
5. Results 3
6. Discussion 9
7. Recommendations 10
8. Conclusions 10
9. Future Work 10
10. References 11

Appendix 4

Development of the Proposed Process. 67

1. Introduction 1
2. Experimental 1
3. Table 1 2
4. Table 2 3
5. Table 3 4
6. Steps of Process 5

List of Figures and List of Tables

Appendix 2 ____ 39

Figure 1 - Flowsheet, drawing 1300-004 (In back pocket)
Figure 2 - Flowsheet, drawing 1300-003 (In back pocket)

Appendix 3 ____ 53

Table 1 P.3
Table 2 P.4
Table 3 P.5
Table 4 P.7
Table 5 P.8

Appendix 4 ____ 67

Table 1 P.2
Table 2 P.3
Table 3 P.4

Acknowledgements

| | Financial Contribution |
|---|---|
| Tetra Process Technologies | 0.00 |
| W.J. Wilson and Associates | 13,000.00 |
| Lapadco. Inc. | 13,000.00 |
| Department of Natural Resources (VAMP) | 26,000.00 |

# 1.0 INTRODUCTION

## 1.1 Objective

The objective of the work is to study a new approach to ion-exchanging processing with slightly soluble industrial minerals which consists in mixing equal molar amounts of resin and mineral to substitute the resin ion with mineral ion, thereafter to process the treated resin to strip the anion form of the resin with a soluble mineral, such as salt, to generate the desirable product. This part of the operation will be done in a columnar operation after exchange in the first instance in the bulk mixture. Separation of resin, residues, and fluids, will be by appropriate screening.

## 1.2 Scope

The scope of the work was to devise an ion-exchanging technique suitable for processing slightly soluble minerals into products such as sodium hydroxide, potassium hydroxide, sodium carbonate, and potassium carbonate. It was anticipated, based on data received from Tetra Technologies, that this would be a straight forward process, but unfortunately the projections produced by Tetra proved to be in error, and we had to return to doing this work on a fixed bed system which had proved to be successful when using 0.1% slurries, and we had to find out exactly how to manipulate 4% slurries to achieve the objective. In a course of which it has been necessary to do a detailed study of the mechanism of ion-exchange using lime or other slightly soluble mineral. This somewhat extended the time involved in the study, but we now have reached a conclusion that this is possible.

## 1.3 Background

The background of the project was that by using 0.1% slurries we where able to generate 8% caustic using the Higgins Loop and also by using the fixed bed system, again using a 0.1% slurry, we were able to achieve levels of caustic up to 11.5%. How this was developed as the process studies went on is detailed in other reports, but we are confident that the objectives can be met by modification of the technique, either using fixed bed or Higgins Loop.

## 2.0 Project Methodology

The method to be used in the process was to take an Amberjet 4600 Cl anion exchanger. This was chosen because of the favourable characteristics between chloride and hydroxide exchange. The resin was packed into a column and treated in turn with the various reagents, starting with lime slurry. The target being 4% lime, which had been screened through a 60 mesh screen, therefore it would pass through the resin column without problem. The effluents were recovered in suitable sized fractions, depending on the concentration of the material emerging, and they were analysed as follows.

Hydroxide - acid based titration with phenolphthalein.

Chloride - silver nitrate/potassium thiocyanate reverse titration.

Lime - by the conventional sugar analysis which ends up as an acid based titration.

The lime treatment was followed by the caustic tails produced in the system and this resin strip solution was followed by a product strip solution which consisted of the effluent from the resin strip to which has been added appropriate levels of sodium or potassium chloride.

The calculations of the results followed the general stoichiometric system giving results in equivalents of the component in equivalents per litre. That enabled us to determine the concentration of the product and the extent to which the resin was being utilized in the loading cycle. All these results are presented in tables in the appendices.

Another aspect of this is of course what do we do with the residues that remain unreacted and the residues that are unable to pass a 60 mesh screen. An analysis of this showed it to be fairly high in lime and we propose that this should be mixed with calcium chloride effluent, treated with acid to dissolve, and therefore get a much higher level of calcium chloride than is obtainable in the process. This possibility will have to be calculated in terms of its economics. The net effect will be that we will have a process that produces no waste, apart from a slight amount of acid insolubles, principally silica.

## 3.0 Results and Discussion

The detailed results are given in the appendices, along with a great deal of data. However we can report that the Higgins Loop experiments were not successful in that we only got 4% caustic as the product. We consider however that they were not especially willing to modify the process to achieve the desired result, and in consequence of which we withdrew from the study and returned to NB to pursue our line of research, following on from our fixed bed work. The first part of this work elucidate the mechanism by which the lime resin interchange occurs and this has been discussed in Appendix 2 and additional information is given in Appendix 3. Basically the reaction is one which hinges on the lime going into solution as it is displaced by exchange, but there is a limit on the amount of hydroxide ion that will go on the resin, with lime as a source, so we devised a second step in the process which is called the resin strip, where we increase the level of hydroxide ion on the resin by using the dilute caustic fractions produced in the cycle. Very satisfactory levels of chloride are displaced from the resin by these means.

In Appendix 4 we introduced a new approach since we found that lime mixed with resin, initially stirred to disperse, then allowed to sit for periods of 1 to 2 hours, gave around 16% of hydroxide on the resin, and this seemed to be a simpler way of overcoming the time constraints involved in the ion-exchange. This work is continuing and we are setting up for ongoing work on a three column system, containing around 6 feet of resin, to give a final in-laboratory test on the system. This will also give us the data we need for plant projections and quantities for a material balance.

## 4.0 Conclusions and Recommendations

We conclude that we can devise an effective process based on the work described above and in the Appendices and will continue to work as described in the Results and Discussion section. We do not anticipate to complete all this work before the end of the project, but are confident we will have a viable process. Some preliminary work has been done on the carbonate system, which is also going well.

References in this "The Final Vamp Report"

1. Tetra Process Technologies Report, "Caustic Production from Lime and Brine." Jan.8 to 18, 2000. Appendix 1.

2. "The Manufacture of Caustic Alkali from Lime and Salt by Ion Exchange. Studies with Tetra Technologies Pilot Plant in Clinton, Tennessee." W.J. Wilson, Feb.7, 2000. Appendix 2.

3. "Development of a Caustic Process using Fixed Bed Ion Exchanging." W.J. Wilson, Feb. 18. 2000. Appendix 3.

4. "Development of the Proposed Process." W.J. Wilson, March 8, 2000. Appendix 4.

References in Appendix 1

1. I.R. Higgins, et.al., "Caustic Production Pilot Test Report", Tetra Technologies Inc. report for J.D. Irving and W.J. Wilson and Associates, 1991.

2. W.J. Wilson, "Manufacture of Caustic Soda from Lime and Salt by Ion Exchange", W.J. Wilson report, 1996.

References in Appendix 2

1. Tetra Process Technologies Report, "Caustic Production from Lime and Brine", Jan. 8 to 18, 2000.

2. I.R. Higgins, et.al., "Caustic Production Pilot Test Report", Tetra Technologies Inc., 1991.

3. W.J. Wilson, "Manufacture of Caustic Soda from Lime and salt by Ion Exchange: A reexamination of the System." 1996.

References in Appendix 3

1. Mellor, J.W., "Comprehensive Treatise on Inorganic Chemistry", ca. 1920

References in Appendix 4

1. "Development of a Caustic Process Using Fixed Bed Ion Exchange." W.J. Wilson, Feb. 18, 2000.

Appendices

1. Tetra Technologies Report on "Caustic Production from Lime and Brine." Tetra, 2000.

2. "The Manufacture of Caustic Alkali from Lime and Salt by Ion Exchange. Studies with Tetra Technologies Pilot Plant in Clinton, Tennessee." W.J. Wilson, Feb.7, 2000.

3. "Development of a Caustic Process Using Fixed Bed Ion Exchanging." W.J. Wilson, Feb.18, 2000.

4. "Development of the Proposed Process." W.J. Wilson, March 8, 2000.

TETRA Process Technologies
A Severn Trent Services Co.

# Higgins Loop™ Pilot Test Report

# Caustic Production from Lime & Brine

Table of Contents


| | | |
|---|---|---|
| A. | Executive Summary | 1 |
| B. | Background | 4 |
| C. | Process Description | 6 |
| D. | Test Program Description | 8 |
| E. | Conclusions and Recommendations | 14 |
| F. | Appendices<br>Resin Technical Data<br>Individual Test Reports<br>Project Economics | 17 |


Test Conducted in

TETRA Process Technologies Technical Center
Clinton, TN
January 8-18, 2000

Test Performed by

R. S. Dennis
R. A. Robeson
A. Porter (W. J. Wilson & Associates)

## Executive Summary

LAPADCO Inc. and W. J. Wilson and Associates contracted with TETRA Process Technologies to conduct a continuous ion exchange pilot program using TETRA's Higgins Loop™ System for the purpose of developing a process to produce caustic soda (NaOH) from lime (CaO) and brine (NaCl). The pilot program, conducted at TETRA's Clinton, TN technical center in January, 2000, was an extension of development work conducted by W. J. Wilson and Associates over the past decade. Background of process development leading to this pilot program is discussed in the next section.

The Higgins Loop™ System, referred to as the CCIX™ in the past, is a continuous ion exchange contactor that utilizes chemical engineering principles of countercurrent liquid/resin contacting to maximize mass transfer between the two phases making the process more efficient than conventional fixed bed ion exchange contactors. The process is also operated in the continuous mode thus eliminating the need for redundant equipment.

The key objectives of the Higgins Loop™ Caustic Production pilot program were:

1. Produce a concentrated caustic solution, greater than 10% NaOH, making it suitable for use in a pulp & paper mill process.

2. Generate a caustic product with minimum chloride contamination, <0.5% Cl, which would make it acceptable for use in the same process. The NaCl feed stoichiometry to achieve this level would have to be less than 106% so that excess Cl in the product would not exceed the above limit.

3. Produce a concentrated $CaCl_2$ byproduct stream to, 1) minimize water use and waste generation, and, 2) to make the stream economically treatable for making a saleable 38% $CaCl_2$ byproduct. The target effluent strength was at least 7% $CaCl_2$.

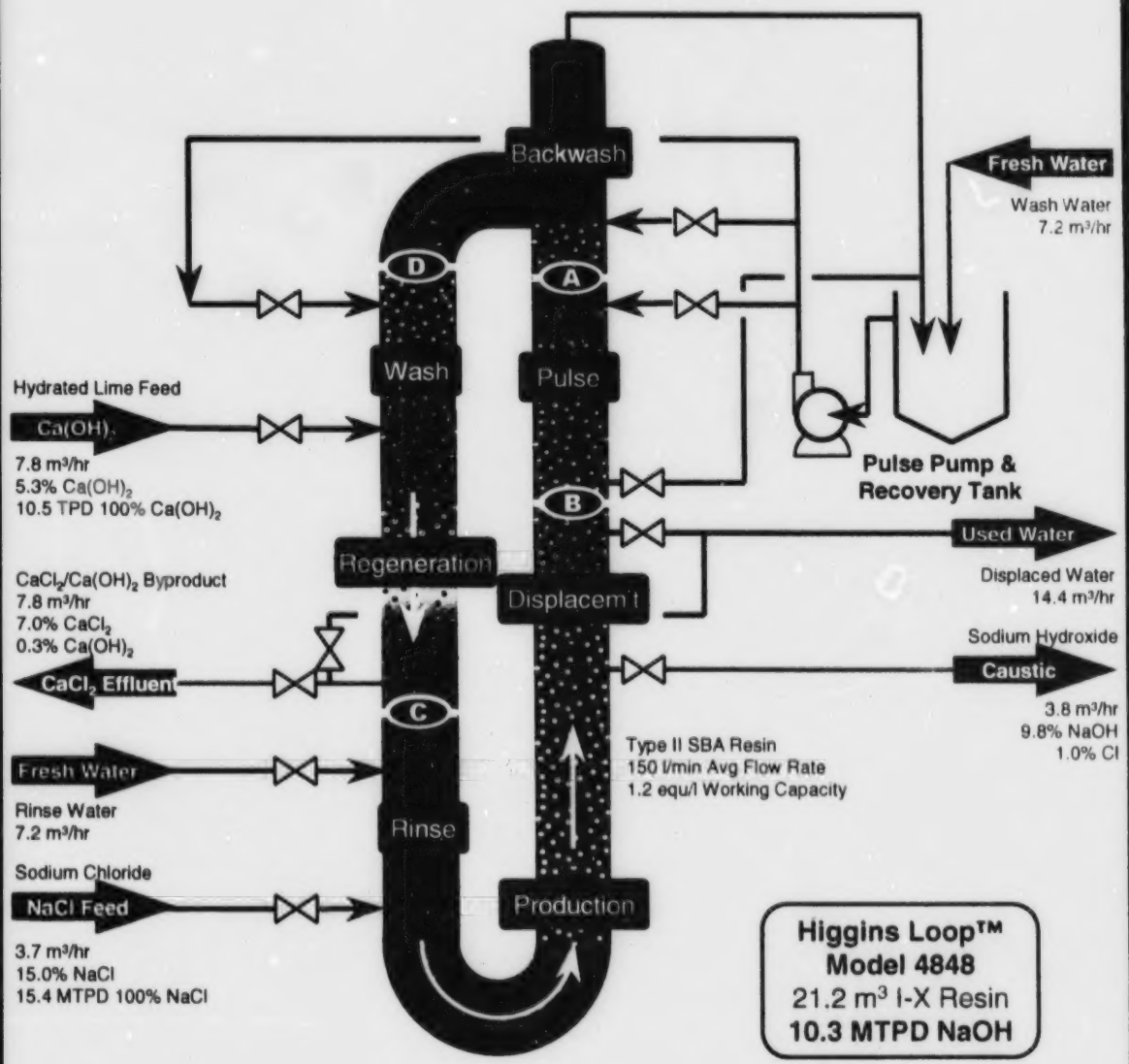
4. Conduct the I-X process with a high resin working capacity, at least 1.1 equ/l utilization. The high working capacity directly relates to high NaOH production capacity per Higgins Loop™ train (contactor). It also affects product purity by minimizing Cl contamination.

The overall Higgins Loop™ process is depicted in Figure 1 showing the target feed and effluent flows and concentrations for a commercial system. The single largest Higgins Loop™ System can process 3,600 MTPY (4,000 STPY) of NaOH based upon a resin working capacity of 1.2 equ/l.

The results of 8 days of pilot and bench testing showed that, although the ion exchange (I-X) process chemistry worked, the process was not efficient enough to be economically viable. The resin could not be regenerated with lime to any greater than 0.55 equ/l OH (42%). The outfall of inefficient resin regeneration in this process include:

1. A larger I-X system would be required for commercial production. A single loop could only process 1,500 MTPY. This results in an additional US$ 40-50/ton of NaOH produced for capital equipment depreciation alone.

**NaOH Production from NaCl & $Ca(OH)_2$**
**via Higgins Loop™ Ion Exchange**
**Pilot Test Program**
**LAPADCO Inc./W. J. Wilson & Associates**




**Commercial Process Flow Diagram**
Figure 1

2. The target NaOH strength of 10% could not be achieved because the salt would have to be further diluted to maintain the minimum relative flow rate through the production zone (reference the explanation for minimum flow on page 14).

3. The NaOH product's Cl concentration target could not be achieved because of its equilibrium concentration in the liquid phase relative to fully regenerated resin was too high to achieve the 0.5% target.

There were other problems associated with the lime regeneration process that were identified but were not considered fatal flaws:

4. Lime feed rate of 110% stoichiometry and 5.3% $Ca(OH)_2$ is insufficient to regenerate the resin to even the levels attained in earlier Higgins Loop™ testing (77%). Only 40% of the lime's OH was exchanged onto the resin.

5. Part of the inefficient lime regeneration is believed to be attributed to the high percentage of undissolved OH ions that are not available as driving force for the ion exchange. This should be quantified in subsequent testwork.

6. Maximum resin regeneration efficiency with lime would require a greater slurry flow rate which would result in a lower effluent $CaCl_2$ concentration. Almost all of the unreacted lime is insoluble and could be recovered for reuse via filtration. The net impact is a minimal increase in lime usage but an additional unit operation (filter) required to separate the fine lime for reuse.

After the fifth pilot test run showed no improvement in system performance, even with replication of some of the work conducted by W. J. Wilson in 1996, both W. J. Wilson and TETRA agreed that continued testing would be futile. It was further agreed to suspend further testing, and TETRA would not charge LAPADCO and W. J. Wilson for the third week of the test program.

Chemical production via ion exchange is a cost effective process for producing high valued products from cheap feedstocks. The process can be conducted more efficiently with a continuous I-X contactor in many applications. The key to economic success in these processes are efficient chemical usage (feed stoichiometry), high product strength and high resin working capacity. The caustic production process requires further bench scale testing, particularly with lime regeneration before it can be commercialized.

## Background

The cyclical supplies and demands for caustic and chlorine, both of which are made via the same process in proportion to each other, has long been a concern to many industrial consumers, including the New Brunswick pulp & paper industry. These chemicals are produced from salt using a chlor-alkali electrochemical process. The major problems with the cycles are that the demand for each chemical is usually out of phase with the other, and the consumers have little control in controlling their prices. The problem is compounded for the pulp & paper industry because they have been large users of both chemicals, but environmental constraints have greatly reduced their consumption of chlorine over the past several years.

W. J. Wilson and Associates approached J. D. Irving, a pulp & paper producer, with a process that would produce caustic via an ion exchange (I-X) process in lieu of the chlor-alkali process. The process produces caustic via exchange of anions from NaCl brine and hydrated lime, $Ca(OH)_2$. A calcium chloride byproduct, $CaCl_2$, is also produced. It was predicted that the process could produce caustic with a strength suitable for use in a pulp & paper mill (10%) and with a chloride content low enough so as not to be deleterious to the process. Being a "production I-X" process that requires strong feed concentrations to minimize dilution, a continuous ion exchange contactor would offer significant chemical and economic advantages over a conventional fixed bed ion exchanger (FBIX) for this application.

W. J. Wilson has long known I. R. Higgins, the inventor of the Higgins Loop™ System, and they have had numerous discussions on how to develop practical processes using ion exchange and the Higgins Loop™. The caustic from lime and brine process was one of them. In 1991, W. J. Wilson and Associates and J. D. Irving contracted with TETRA Technologies, Inc. and I. R. Higgins to pilot this NaOH production I-X process.

TETRA Technologies, Inc. issued a test report[1] upon completion of the pilot test. It generated a caustic solution containing 8% NaOH and 1% Cl. The maximum $Ca(OH)_2$ strength used in the regeneration process, 0.1%, was determined by its solubility which is very low. The lime has to be solubilized in order for the OH ions to be able to exchange with the Cl ions on the resin. Also, there has to be an excess of OH ions in solution to regenerate the resin efficiently. The lime feed contained 85% soluble OH at a feed stoichiometry of 145% required for the exchange. Resin conversion to the OH form was 77% (~1.0 equ/l).

Process development was continued by W. J. Wilson and Associates with emphasis on increasing the NaOH strength and reducing the product's Cl content. Emphasis was also placed on using a much higher $Ca(OH)_2$ feed strength so as to produce a more concentrated $CaCl_2$ byproduct stream that could be treated economically for sale. The results of this work are addressed in a February, 1996 report[2].

Wilson's I-X testwork was conducted using FBIX columns in series mode. Emphasis was placed on maximizing NaOH product strength, minimizing lime feed stoichiometry, minimizing Cl contamination of the NaOH product and using a more concentrated lime slurry to generate a $CaCl_2$ stream that could be economically evaporated into a 38% $CaCl_2$ byproduct. The testwork showed that an 11.5% NaOH product containing 0.8% Cl could be produced using a Type II resin.

W. J. Wilson & Associates met with TETRA Process Technologies in September, 1999, to discuss the results from the aforementioned testwork and to review the overall economics of the caustic production process.

TETRA indicated that the process economics were favorable providing that caustic could be used as a 10% solution, the lime and brine could be used at no greater than 110% of stoichiometric usage, the resin utilization, or working capacity, would be high, and that the resin could be regenerated well enough to keep the Cl level in the product no greater than 1%. A single Higgins Loop™ Unit could process 3,600 MTPY NaOH (4,000 STPY) based upon a resin working capacity of 1.2 equivalents per liter (equ/l). The project economics for 2 cases are tabulated in Appendix C.

## Process Description

Caustic production from lime and brine is termed an I-X production or metathesis process, conversion of an alkali, salt or acid from one form to another by switching either the anions or cations from 2 respective chemicals. In caustic production, the more valuable anion from hydrated lime, calcium hydroxide, is exchanged onto an anion resin loaded with chloride anions. Resin containing hydroxide ions is then contacted with brine, sodium chloride, where the process is reversed by exchanging chloride anions onto the resin. Hydroxide enters the solution to form sodium hydroxide, a chemical of much greater value than either lime or brine.

**Process Chemistry**: A "Cl-loaded" resin is contacted with a slurry of $Ca(OH)_2$ to convert the resin from its chloride form to its hydroxide form. This I-X reaction, referred to as **regeneration**, is:

Regeneration: $Ca^{2+} + 2OH^- + 2R\text{-}Cl \longrightarrow 2R\text{-}OH + Ca^{2+} + 2Cl^-$

where "R" is the anion resin. The products from this reaction are "OH-regenerated" resin and $CaCl_2$ solution. If it is relatively concentrated, the $CaCl_2$ can be further processed into a saleable byproduct. Only dissolved OH ions are available for exchange with the Cl-loaded resin. Solid $Ca(OH)_2$ present in solution will not react with the resin. Its solubility in water is 0.1%.

OH-regenerated resin is then contacted with a concentrated NaCl solution to complete the process. The resin is converted back to its Cl form, and the desired chemical, NaOH (caustic soda), is produced in the **production** reaction:

Production: $Na^+ + Cl^- + R\text{-}OH \longrightarrow R\text{-}Cl + Na^+ + OH^-$

The concentration of the NaOH product is important and is controlled primarily by the NaCl feed concentration which has a solubility of 26% at ambient temperatures. Theoretically, a 26% NaCl solution could be converted to an 18% NaOH solution.

The efficiency of each reaction is determined by the amount of chemical needed to contact the resin to fully convert the resin relative to the theoretical amount needed for the exchange. This is called feed **stoichiometry** and is the driving force to complete the reaction. Unused chemical (Cl or OH) not reacted because the stoichiometric amount is greater than 100% remains in solution and exits the process as a contaminant in the products. A Type II strong base anion resin was selected for this process to minimize the feed stoichiometries in both I-X reactions.

**The Higgins Loop™ Process**: The Higgins Loop™ continuous, countercurrent ion exchange contactor is configured for the caustic production process as depicted in Figure 1. Lime (CaO) is "slaked" and fed as hydrated lime slurry into the loop's regeneration vessel. In the original Higgins Loop™ pilot testwork conducted by I. R. Higgins in 1991, the slurry's strength was controlled at slightly more than its solubility, or ~0.2%. Based upon subsequent work by W. J. Wilson & Associates, the slurry strength was controlled at 5.3% $Ca(OH)_2$ (4.0% CaO) and a feed stoichiometry of 110%.

Specific flow rate of lime through the regeneration zone of the pilot loop was 6.4 cm/min (1.6 GPM/Ft²), and the residence time in the resin was 12 minutes. Assuming the I-X reaction

worked as predicted, the $CaCl_2$ effluent would exit this zone as a 7.7% solution, high enough for economical evaporation to a 38% $CaCl_2$ byproduct.

OH-regenerated resin exiting the regeneration zone is washed with process water to displaced entrained lime slurry and push it back into the regeneration zone. Wash water in this resin does not dilute the lime, but is transferred with the resin above "D" valve into the backwash zone in a subsequent pulse.

Regenerated resin is backwashed of any fines or solids and is then dropped through "A" valve into the pulse vessel. The resin was "pulsed" on 4-minute cycles. Resin is hydraulically moved below "B" valve in measured batches. This resin contains water which is removed from the resin in the displacement zone so that it does not dilute the NaOH product.

Fresh water is used for multiple purposes in the Higgins Loop™. First, it is used for washing lime from the resin, then the same water is used for resin backwashing, and finally, it is used for pulsing the resin through the loop. It exits the loop as "displaced water". This water could be used for lime dilution in the commercial process. It has nil effect in diluting either lime or caustic.

15% NaCl is fed into the loop's production zone at a feed stoichiometry of 110%. Its strength is determined by the minimum allowable flow rate relative to the average resin rate. This rate is 0.4 bed volumes (BV's). Any lower rate would not displace liquid entrained in the resin resulting in brine and product losses. At 15% feed strength, the product was estimated to contain 10% NaOH.

Cl-loaded resin exiting the production zone was rinsed with a second stream of fresh water to recover NaCl entrained in it back into the production zone. Used rinse water moved with Cl-loaded resin in subsequent pulses above "C" valve into the regeneration zone. This water would be displaced from the loop by $CaCl_2$ solution to avoid dilution of that effluent. (The pilot unit was not initially configured to separate used rinse water from $CaCl_2$, but this change would be made in later test runs).

## Test Program Discussion

The actual testing was started on Jan 11 with the Higgins Loop™ pilot system configured for producing caustic from lime and brine as illustrated in Figure 2. A Higgins Loop™ pilot unit consists of a 2"-Ø resin loop. Each resin pulse consists of 600 mls. It takes about 2¼ hours to circulate the resin completely through the loop using 4 minute service cycles. The resin used in the loop was Dowex Marathon A2, a monospheric Type II resin in the Cl form (see resin data sheet in Appendix A). The key variables for the first few runs were:

- Lime Slurry Regenerant – 5.3% $Ca(OH)_2$ (4.0% CaO) concentration and feed stoichiometry of 110% needed to regenerate the resin with 1.1 Equ/l of OH ions.
- Sodium Chloride Feed – 15.0% NaCl concentration, high enough to produce 9.8% NaOH, at a feed stoichiometry of 110% needed to convert the resin with 1.1 Equ/l of Cl ions.
- Resin Working Capacity – 1.1 Equ/l equating to 1.1-1.2 Equ/l of OH regeneration and 1.1-1.2 Equ/l of Cl loading in the production zone.

The system was operated for 4 hrs on the Jan. 11 afterwhich 2 key samples were pulled to quantify performance. The OH-regenerated resin assayed 0.47 equ/l OH indicating that 35% of the resin was regenerated to its OH form, a measure of its working capacity. Secondly, the product assayed 1.5% NaOH which meaning that the I-X process was working after only a few hours of operation. It takes about 2 hours to move the resin completely through the loop.

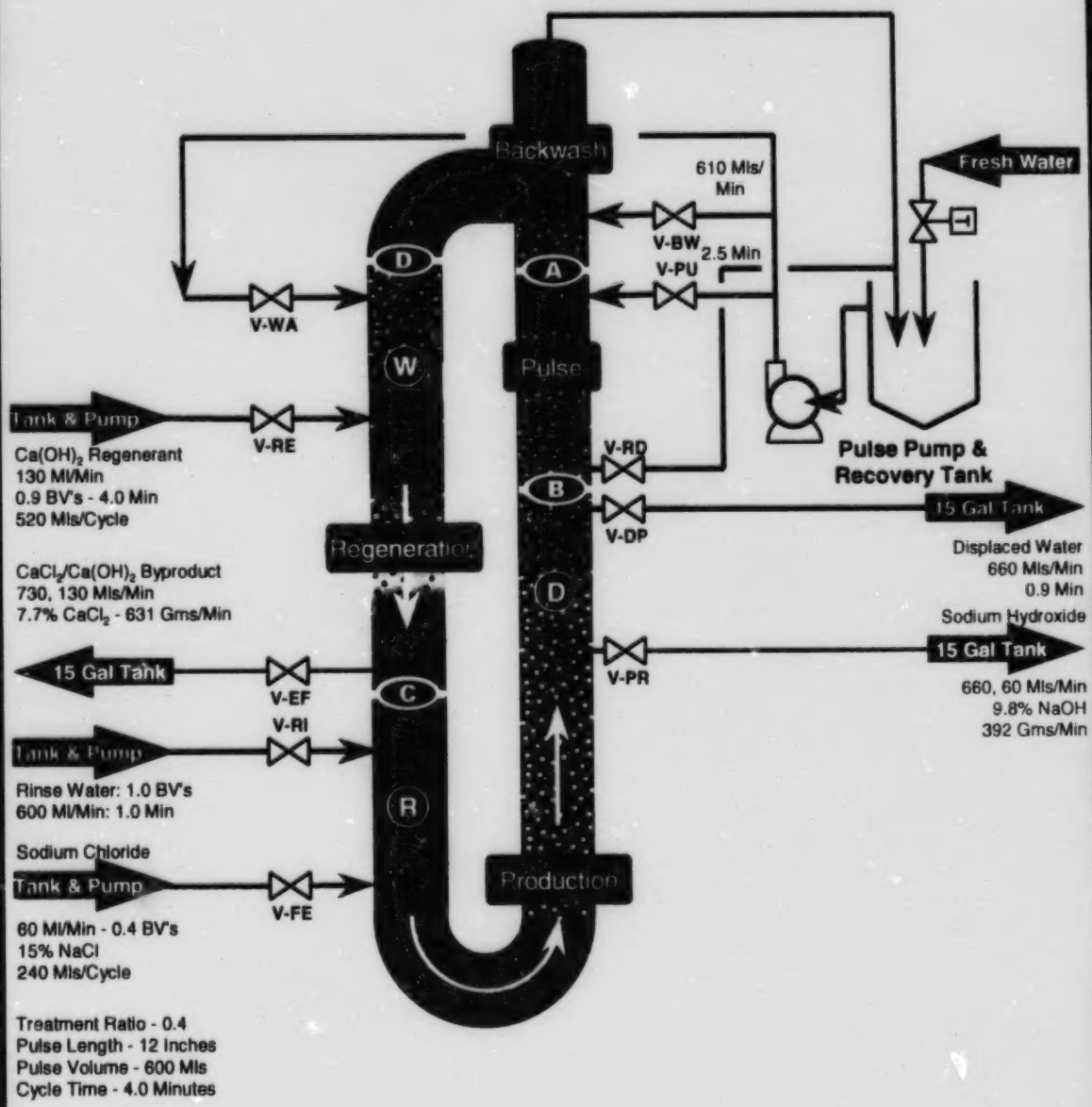
Resin working capacity is a direct measurement of NaOH production capacity; the higher its capacity, the greater the NaOH production capacity per Higgins Loop™. The basis used for preliminary design was 1.2 equ/l which equates to 3,600 MTPY 100% NaOH per Model 4848 Higgins Loop™, the largest single system capacity.

**Run #01**: The system was operated for 5½ hours on the second day, the first quantified test run. A material balance was conducted during the final 70 minutes of the run. The OH-regen'd and the Cl-loaded resins assayed 0.55 and 0.05 equ/l OH, respectively. The net resin working capacity was 0.50 equ/l or 38% of total capacity. The NaOH product assayed 2.6% NaOH and 5.0% Cl. Preliminary assessment indicated that the resin could not be regenerated beyond 40% of its total capacity with the lime slurry. Reference Run #01 data sheets in Appendix B.

**Run #02**: The flow configuration remained the same as originally designed. $Ca(OH)_2$ and NaCl feed strengths and flows remained the same. The system was operated for 3½ hours with a material balance period of 70 minutes. The OH-regen'd and the Cl-loaded resins assayed 0.36 and 0.03 equ/l OH, respectively, indicative of a working capacity of 0.33 Equ/l (25% of total). The NaOH product assayed 3.0% NaOH and 5.5% Cl. Reference Run #02 data sheets in this section. The lime slurry flowrate was slightly "starved" during this test run which could explain the reduced OH-regen'd resin conversion. Reference Run #02 data sheets and Figure 3 the latter of which quantifies performance in flow diagram format.

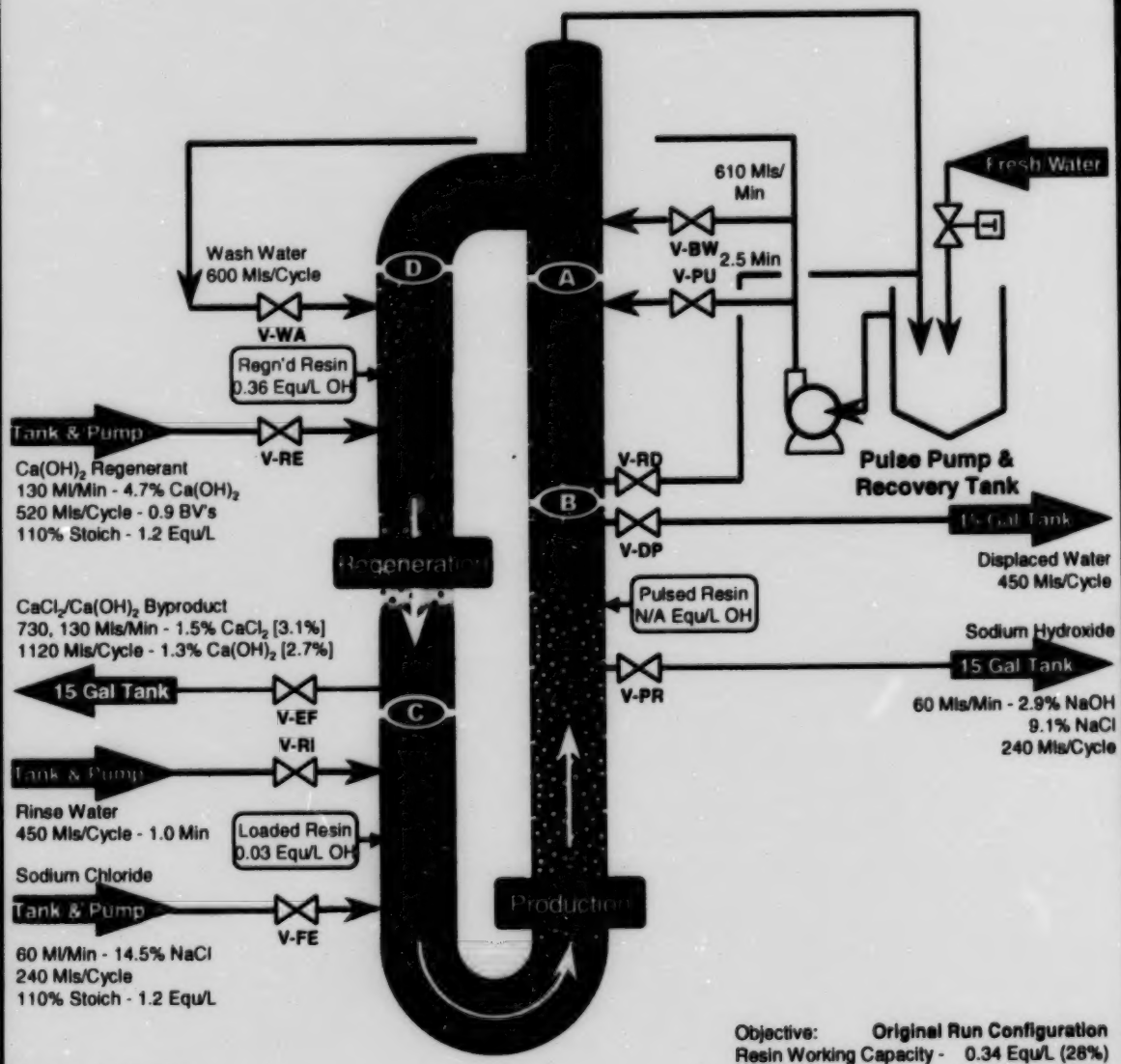
**Run #03**: This was the final run in the original flow configuration. The major change was to use diluted $Ca(OH)_2$ (2% CaO) at twice the flow rate to determine if lime dilution could positively affect the resin OH regeneration process. Lime feed stoichiometry was also increased slightly to assist in improving regeneration. The results of the test run, conducted for 4¼ hours, showed no significant increase in resin conversion. The OH-regen'd assayed 0.45 Equ/l (35%). NaOH product increased slightly to 3.4%. Reference Run #03 data sheets in Appendix B.

**NaOH Production from NaCl & $Ca(OH)_2$**
**via Higgins Loop™ Ion Exchange**
**Pilot Test Program**
**LAPADCO Inc./W. J. Wilson & Associates**




**2"-Ø Pilot Loop Configuration**
Figure 2

## NaOH Production from NaCl & $Ca(OH)_2$ via Higgins Loop™ Ion Exchange Pilot Test Program LAPADCO Inc./W. J. Wilson & Associates




**Pilot Test Run #02 - 13 Jan 00**

Figure 3

Following the test run, TETRA and W. J. Wilson & Associates assessed the continuous I-X pilot program progress and compared it with fixed bed column testwork conducted by W. J. Wilson in the past. W. J. Wilson pointed out that, in their FBIX work, they utilized a portion of NaOH product to complete the resin conversion to its OH form, a process termed "scrubbing". Secondly, W. J. Wilson added some NaOH product to the NaCl feed in order to indirectly fortify the final product.

TETRA determined a method of implementing both changes into Run #04. Some NaOH product and NaOH flake would be added to the pulse water system to simulate scrubbing the resin exiting the $Ca(OH)_2$ regeneration zone. Also, using some product generated in Run #03 and some solid NaCl, the NaCl feed would be fortified.

TETRA noted that the net working capacity of the resin would not be increased by this change and that, if it remained the same as previous runs (<0.5 Equ/l) that the commercial system capacities would be less than 50% of the 4,000 STPY design. Secondly, it was noted that addition of NaOH to the NaCl could reduce the resin's working capacity due to a shift in equilibrium between the brine and the Cl-loaded resin.

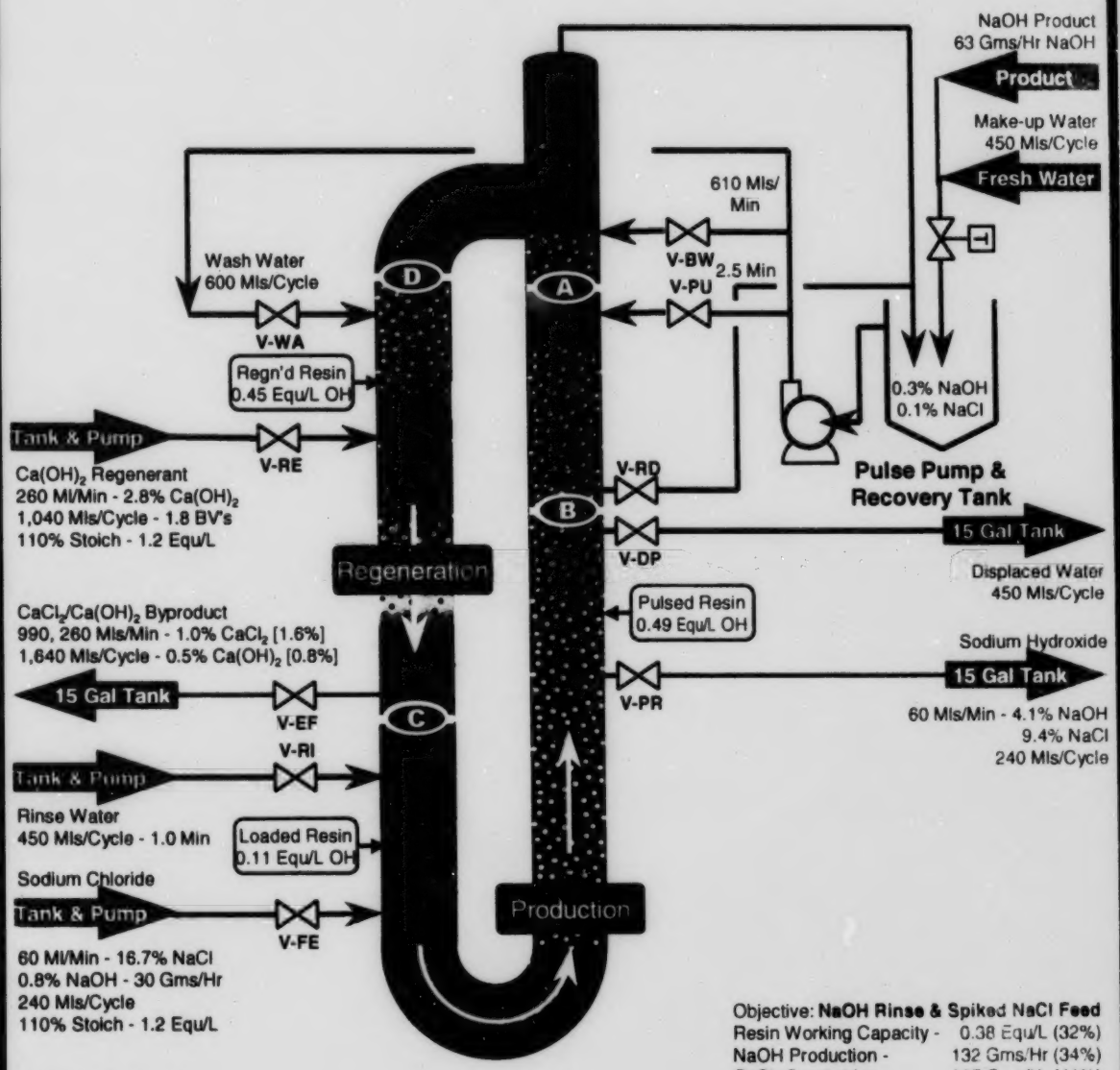
**Run #04**: The NaCl feed contained 16.6% NaCl and 0.8% NaOH, high enough to produce 11% NaOH if the overall I-X process worked efficiently. Enough product and flake was added to the 200 l pulse water system to raise its concentration to 0.3% NaOH. The pilot unit was operated for 3¼ hours during this run. The resin exiting the $Ca(OH)_2$ regeneration zone assayed 0.45 Equ/l (35%). An new resin sample was pulled from the bottom of the pulse vessel to quantify the performance of resin scrubbing in the wash and backwash zones. This resin assayed 0.49 Equ/l (38%) improving the resin conversion by 0.04 Equ/l. Lime feed strength was maintained at 2% CaO for Runs #04 and #05.

The product exiting the loop contained 4.1% NaOH. Backing out the feed NaOH, the net increase in concentration was 3.3%, assuming there was no dilution in the production zone. The Cl-loaded resin assayed 0.11 Equ/l OH during this run, up from 0.03-0.05 Equ/l in the 3 prior runs. This 0.07 Equ/l increase was attributed to adding NaOH to the NaCl feed. It's net effect is to reduce the resin's working capacity. Reference Run #04 data sheets and Figure 4 which quantifies performance in flow diagram format.

**Run #05**: The pilot unit was operated in the same mode as that of Run #04 for 4 hours to determine if any improvements would result or to confirm the results of that run. The feed contained 14.9% NaCl and 1.1% NaOH. The pulse water assayed 0.4% NaOH. The OH-regenerated, OH-scrubbed and Cl-loaded resins assayed 0.51, 0.44 and 0.17 Equ/l, respectively. The results indicate that scrubbing had nil effect on resin conversion, and the NaOH in the feed reduced the resin conversion to its Cl form.

Recognizing the fact that dilute NaOH scrubbing was not improving resin conversion to the OH form substantially, it was decided to conduct a series of column tests to quantify resin conversion with NaOH while also determining what concentrations and flows would be required in a commercial system to generate the program's objectives. A resin regeneration efficiency test was conducted in a laboratory column using a sample of OH-regenerated resin from the pilot column.

## NaOH Production from NaCl & $Ca(OH)_2$ via Higgins Loop™ Ion Exchange Pilot Test Program LAPADCO Inc./W. J. Wilson & Associates




**Pilot Test Run #04 - 15 Jan 00**

Figure 4

The resin, containing 0.53 equ/l OH, was treated with 200% stoichiometric amount of 2N NaOH required to complete the regeneration. The effluents were collected and analyzed for Cl and OH. The treated resin was also analyzed. The results below in Table 1 show that the resin could only be regenerated to 72% of its total capacity with NaOH based upon the resin assay. Using the composite analysis, the resin was 83% regenerated. The test results show that the resin cannot be fully regenerated without a large excess of OH ions.

**Resin Regeneration Efficiency**

| | | Chloride | | Hydroxide | |
|---|---|---|---|---|---|
| | Volume | Meq | Equ/L | Meq | Equ/L |
| Pilot Regenerated Resin | 50.0 | 33.5 | 0.67 | 26.5 | 0.53 |
| NaOH Feed (200% Stoich @ 2N) | 40.0 | | | 80.0 | |
| | | | | | |
| Caustic Effluents | 10.0 | 1.5 | 0.15 | 2.4 | 0.24 |
| | 10.0 | 4.4 | 0.44 | 7.9 | 0.79 |
| | 10.0 | 4.6 | 0.46 | 12.2 | 1.22 |
| | 10.0 | 3.9 | 0.39 | 15.3 | 1.53 |
| | | 3.0 | 0.30 | 7.7 | 0.77 |
| Rinse Water Effluent | 250.0 | 7.5 | 0.03 | 18.8 | 0.08 |
| Effluent Composite | | 24.9 | | 64.3 | |
| | | | Equ/L | | Equ/L |
| Resin Analysis Based on Composite | | | 0.172 | | 0.845 |
| Actual Resin Analysis | | | 0.300 | | 0.770 |
| | | or | 28% | | 72% |

Table 1

Individual test summaries and analytical data for Runs #01-05 can be found in Appendix B.

## Conclusions & Recommendations

The caustic I-X process cannot produce the target caustic soda quality (strength & purity) with the current resin regeneration process. The findings of the pilot test program were stated in the executive summary on pages 1 and 3 and are not restated here. The caustic production process requires further bench scale testing, particularly with lime regeneration before it can be commercialized.

More detailed study and testing on the resin regeneration process needs to be done to make the process economical. There needs to be a high dissolved OH concentration present in the slurry feed in order to effectively regenerate the resin. "Scrubbing" (described below) with NaOH should be limited to converting the final 10% of resin to its OH form. Otherwise, resin working capacity is reduced and capital costs are increased. Recovery of unused lime from the $CaCl_2$ effluent is economically important.

Equilibrium testing should be conducted on regenerated resin and NaCl/NaOH solutions to predict the Cl levels in NaOH product attainable in a dynamic I-X process. Stoichiometric usage of NaCl is very important as noted below in the caustic scrubbing model because any unexchanged Cl reports to the NaOH product.

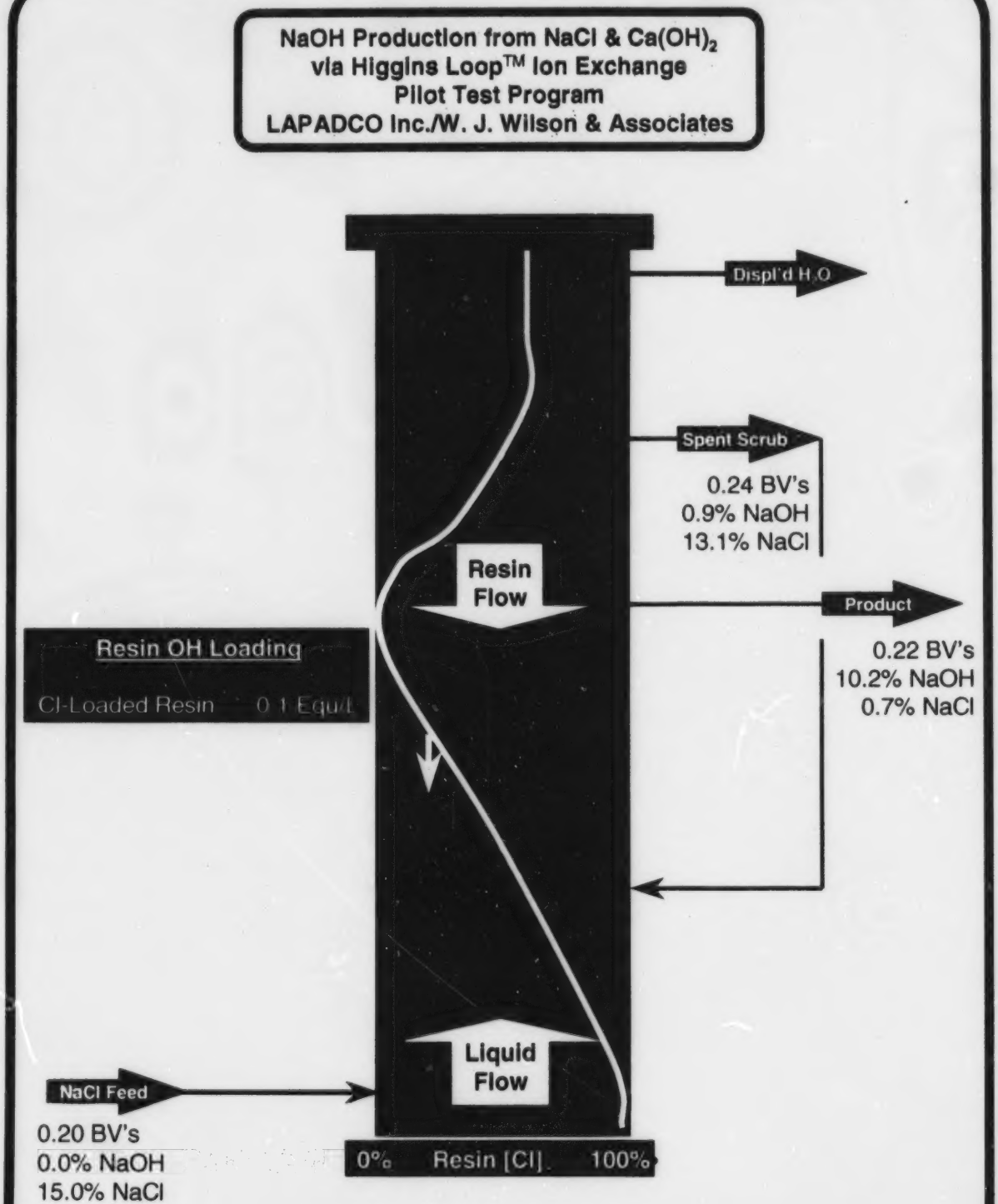
The use of water as a barrier between the 2 chemical phases for regenerated resin washing and loaded resin rinsing had no effect on the respective ion exchange processes.

Type II SBA resin has always been used in NaOH production testwork due to its ease of regeneration. The above regeneration and production column testing should be conducted with Type I resin in parallel to determine if it offers any benefits to the overall process.

Caustic Scrubbing: The only manner in which to produce a concentrate caustic solution with minimum Cl contamination is to ensure that the resin entering the NaOH production zone is fully regenerated (~95% converted) and to use no more than 105% of stoichiometric NaCl feed. Otherwise, the 2 phases reach an equilibrium with each other that precludes further Cl exchange to the resin phase. If the resin cannot be effectively regenerated with lime, there is a mechanism that could be employed in the Higgins Loop™ to maximize conversion of the resin using a slip stream of NaOH product. This will only work if the equilibrium between NaOH product and regenerated resin will keep the liquid Cl phase concentration below the target concentration. This could not be demonstrated during the pilot program.

The process is termed "Scrubbing" and has been utilized in other Higgins Loop™ processes to improve the purity of products from the loop. It is a TETRA proprietary process. The NaOH "Scrubbing" process requires a zone above the product outlet and below the pulse water displacement. It is designed to allow some of the product to flow above the outlet and complete the regeneration of the resin that lime could not effect. Spent scrub solution is withdrawn from the loop and reinjected in the production zone, downstream of the NaCl feed inlet. In this manner, resin conversion to the Cl form is maximized because there is no NaOH in the feed to adversely shift the phase equilibrium and reduce conversion efficiency in the production zone

An example of the scrubbing process is depicted in Figure 5, a conceptual production zone profile. The profile shows the feed, product and scrub stream flows relative to the resin flow (in terms of BV's).




**Conceptual Production Zone Profile**
Figure 5

The process is depicted for a case where the resin's working capacity is 0.5 equ/l, roughly that of the pilot program results. The profile serves as a graph of resin [OH] and [Cl] in the column.

The continuous I-X process cannot perform physically as depicted in Figure 5 even if the phase equilibrium allows for generation of a low [Cl] NaOH product. The relative liquid flow rates are far below the minimum 0.4 BV's required to advance the liquid through the porous resin. Below this value, there is not enough liquid flow to counter the resin flow and its associated liquid entrainment.

A model of the production/scrubbing zone profile was designed to show the effects of resin working capacity, NaCl feed stoichiometry and concentration on relative flow rates. The results of several conditions are compiled in Table 2.

| Conditions | NaCl Feed | | | Resin Working | NaOH Product | | Capacity |
|---|---|---|---|---|---|---|---|
| | Stoichtry | %NaCl | Flow(BV's) | Capacity | %NaOH | %NaCl | per Loop |
| A NaCl Feed - 15% CH Resin - 1.25 | 105% | 15.0% | 0.44 | 1.20 Equ/L | 10.2% | 0.7% | 10.3 MTPD |
| Increase NaCl Feed Stoichiometry | 110% | 15.0% | 0.46 | 1.20 Equ/L | 9.7% | 1.4% | 10.3 MTPD |
| Increase NaCl Feed - 17% | 105% | 17.0% | 0.39 | 1.20 Equ/L | 11.7% | 0.9% | 10.3 MTPD |
| B NaCl Feed - 15% CH Resin - 1.00 | 105% | 15.0% | 0.35 | 0.95 Equ/L | 10.2% | 0.7% | 8.2 MTPD |
| Increase NaCl Feed - 17% | 105% | 17.0% | 0.31 | 0.95 Equ/L | 11.7% | 0.9% | 8.2 MTPD |
| C NaCl Feed - 15% CH Resin - 0.60 | 105% | 15.0% | 0.20 | 0.55 Equ/L | 10.2% | 0.7% | 4.7 MTPD |
| Increase NaCl Feed - 17% | 105% | 17.0% | 0.18 | 0.55 Equ/L | 11.7% | 0.9% | 4.7 MTPD |

NaOH Production Zone Flows, Concentrations & Capacities
Table 2

Case A shows the target conditions set in Figure 1 (Page 2), namely 1.2 equ/l working capacity, 15% NaCl feed and 110% of stoichiometric feed. The relative flow rates are above 0.40 BV's for 2 variations of Case A, 105% and 110%. Increasing the %NaCl produces a more concentrated product, but the relative flow rate is just below the threshold.

The model was redone (Case B) to incorporate the results of earlier Higgins Loop™ testing (1991) which had a regenerated resin conversion of 77%. 0.1% CaO solution was used in this test at a flow rate 40 times greater to obtain the higher degree of conversion. The relative flow rates are further below the 4.0 BV threshold in order to obtain the 10% product strength. This is why they were only able to achieve 8% NaOH in that program – the NaCl had to be diluted to maintain the minimum flow.

Commercial conditions for the current process are shown in Case C where the OH-regenerated resin is 45% converted. The flow rates are greatly reduced to maintain product strength. Single loop capacity is also reduced to 45% of target capacity.

## Appendices

A. Resin Technical Data

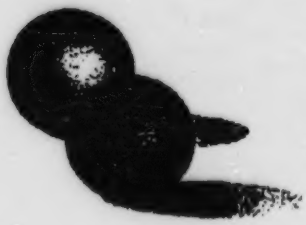
B. Individual Pilot Test Reports

C. Project Economics

## References

1 I. R. Higgins, et. al., Caustic Production Pilot Test Report, TETRA Technologies, Inc. report for J. D. Irving and W. J. Wilson & Associates, 1991

2 W. J. Wilson, Manufacture of Caustic Soda from Lime and Salt by Ion Exchange, W. J. Wilson report, 1996



# DOWEX MARATHON A2 Type II Anion Resin

*An efficient, uniformly sized, high capacity resin for demineralization*

## Description

DOWEX* MARATHON* A2 resin is a high capacity, gel-type, strong base Type II anion exchange resin of narrow bead size distribution. It is based on a styrene-divinyl benzene copolymer matrix with quaternary ammonium functional groups. It is particularly well suited for demineralizing water with a high percentage of mineral acids. This Type II anion exchange resin is specifically designed to give high throughput and economical operation in demineralizer systems. Because of its uniform particle size, this resin offers a number of economic advantages over conventional (Gaussian-distributed) resins.

The small uniform bead size of DOWEX MARATHON A2 resin results in rapid exchange kinetics during operation, more complete regeneration of the already efficient Type II anion resin, and faster, more thorough rinse following regeneration. It can be best used for water with a high percentage of mineral acids (chlorides and sulfates)—where silica and carbon dioxide make up less than 25% of the anions in the feedwater. Operating temperature should not exceed 95°F.

DOWEX MARATHON A2 anion resin is supplied in the chloride form. The physical and chemical properties are listed in Table 1. The suggested operating conditions and parameters for use of DOWEX MARATHON A2 in demineralizer operation are summarized in Table 2.

*Trademark of The Dow Chemical Company

## High Operating Capacity

Type II strong base anion resins are different from Type I strong base anion resins in that their functional group (dimethylethanolamine) is less basic. As a result, regeneration is more efficient and operating capacities are higher. Because DOWEX MARATHON A2 is a uniform bead size resin, its regeneration efficiency is higher, producing added capacity. Thus the practical operating capacity of DOWEX MARATHON A2 is the highest of all strong base anion resins. This combination of high total capacity and superior regeneration efficiency can equate to longer runs, increased throughput, and lower operating costs.

## High Regeneration Efficiency

The bead size uniformity of this resin results in exceptionally efficient regeneration. Since there are no oversized beads present, all the resin beads finish regeneration at approximately the same time. The regeneration procedure does not waste caustic soda waiting for large beads to regenerate. Utilization of the regenerant is therefore better. This can mean lower operating costs and reduced waste disposal costs. In addition, the excellent regeneration efficiency of DOWEX MARATHON A2 can result in better removal of silica from water than conventional Type II anion resins.

## Faster Rinse With Less Water

The absence of oversized beads means rinse time and rinse water requirements are reduced. The sharper wave front resulting with the uniform sized resin beads means less rinse water will be required. In some plant operations, DOWEX MARATHON A2 has reduced rinse time by more than 40%. This can further reduce operating costs and time off-line.

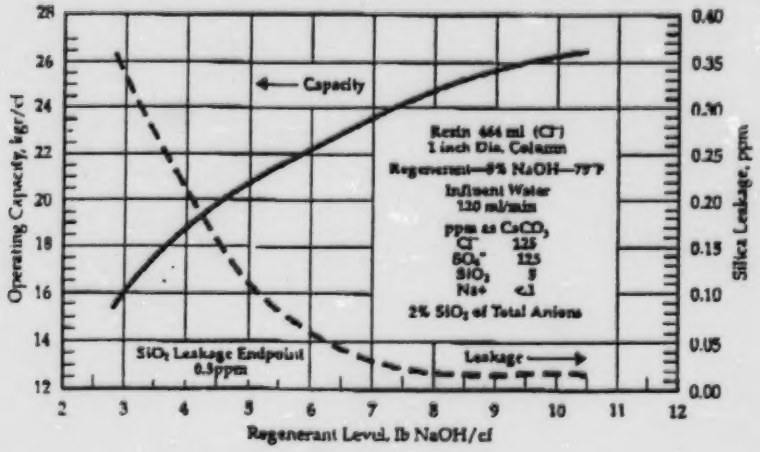
# PROPERTIES AND OPERATING INFORMATION

*Table 1. Typical Physical and Chemical Properties for DOWEX MARATHON A2 Resin*[1]

| | |
|---|---|
| Physical Form | Hard, cream-colored, spherical beads |
| Chemical Form | Chloride, $Cl^-$ |
| Total Exchange Capacity | 1.3 meq/ml (28.4 kgr/ft³ as $CaCO_3$) |
| Water Retention Capacity | 42% |
| Range | 38–45% |
| Bead Size Distribution | |
| Median Volume Diameter | 550 ± 50 microns |
| Distribution, 95% within | ± 100 microns |
| Nominal Screen Size, mesh | 30/40 |
| % on +25 mesh, maximum | 1% |
| % through +40 mesh, maximum | 1% |
| Specific Gravity | |
| Chloride Form | 1.12, approximately |
| Hydroxide Form | 1.10, approximately |
| Shipping Weight | 43 lb/ft³ (690 gm/l) |
| Whole Perfect Beads | Greater than 90% |

[1]Contact your local technical sales representative to receive updated comprehensive Sales Specification and Material Safety Data Sheets.

*Figure 1. Operating Capacity and Silica Leakage—Effect of Caustic Loading DOWEX MARATHON A2 Resin*




## Operating Capacity and Leakage

Figure 1 shows the operating capacity in terms of kgr/ft³ ($CaCO_3$) of DOWEX MARATHON A2 as a function of caustic soda (sodium hydroxide) regenerant dosages. In addition, the graph indicates the silica leakage based on the regenerant loading. This information will help estimate capacity and leakage.

## Pressure Drop

The pressure drop across a resin bed can vary depending on a number of factors. These include resin type, bead size, interstitial space, flow and temperature. Smaller beads result in greater pressure drop. Uniform beads have greater interstitial space and thus lower pressure drop. How the bed is packed also affects pressure drop. Tighter packing decreases the interstitial space and increases pressure drop. As the temperature of the water increases, viscosity decreases and pressure

*Table 2. Suggested Demineralization Operating Conditions and Parameters for DOWEX MARATHON A2 Resin (Type II)*

| | |
|---|---|
| Maximum Temperature | |
| $OH^-$ Form | 95°F |
| $Cl^-$ form | 175°F |
| pH Range | 0–14 |
| Minimum Bed Depth | 30 inches |
| Service Flow Rate | 2–4 gpm/ft³ |
| Velocity | 4–8 gpm/ft² |
| Pressure Drop | (See Figures 2 & 3) |
| $Cl^-$ Form | 0.3 psi/ft @ 5 gpm/ft², 77°F |
| Backwash Flow Rate | (See Figures 4 & 5) |
| Flow at 50% Expansion, $Cl^-$ | 2.3 gpm/ft² at 77°F |
| Flow at 80% Expansion, $Cl^-$ | 3.7 gpm/ft² at 77°F |
| Regenerant | Typically NaOH |
| Regenerant Level | Dependent on desired capacity and leakage. (See Figure 1) |
| Concentration | 3–4% NaOH |
| Flow Rate | 0.2–0.5 gpm/ft³ |
| Regenerant Contact Time | 45 minutes, minimum |
| Temperature | Ambient, or 95°F for $SiO_2$ removal |
| Rinse Water Requirement | 20–40 gal/ft³ resin |
| Displacement Rinse Rate | 0.2–0.5 gpm/ft³ |
| Fast Rinse Rate | 1.0–2.0 gpm/ft³ |
| Swelling $Cl^-$ to $OH^-$ | 14%, approximately |

drop is reduced. All these factors combined affect the pressure drop in any given system.

The information provided in Figures 2 and 3 show the typical pressure drop values for DOWEX MARATHON A2 anion exchange resin based on flow rate and temperature. Figure 2 shows the pressure drop per foot of resin bed depth when the resin is in either the hydroxide or chloride form. The form of the anion resin has little effect since the change in bead size is relatively insignificant. Normally the pressure drop across a resin bed in demineralizer service is quite low because of the low flow rates utilized.

Figure 3 shows the significant effect of temperature on pressure drop. Demineralizer beds operating during the summer (70°F) at normal flows may experience a 50% increase in pressure drop under winter conditions (35°F).

*Figure 2. Pressure Drop vs. Flow Rate DOWEX MARATHON A2 Resin*

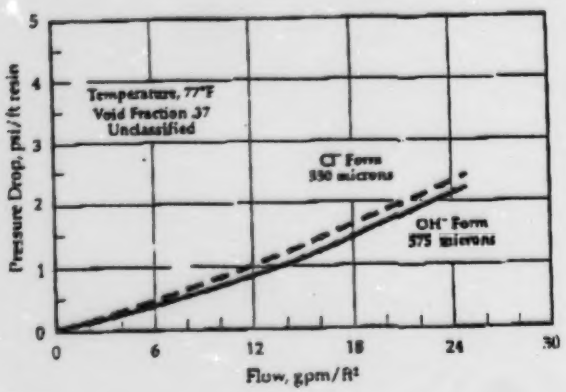
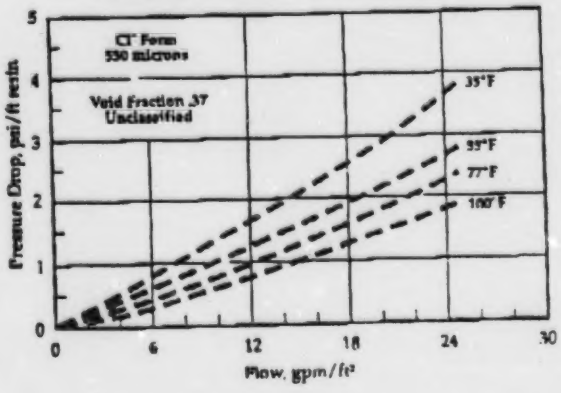



*Figure 3. Pressure Drop vs. Flow Rate— Effect of Temperature DOWEX MARATHON A2 Resin*



# DOWEX MARATHON A2
# Type II Anion Resin



## Backwash Expansion

Backwash expansion data for DOWEX MARATHON A2 resin is presented in Figures 4 and 5. In addition to flow rate, the backwash expansion of resins is affected by the bead diameter, bead density, bead uniformity, and temperature of the water. A uniform bead resin requires less flow to expand to the same height as a Gaussian distributed resin of the same average particle size. DOWEX MARATHON A2 has a smaller average particle size than a conventional Gaussian distributed anion resin. These combined effects mean a lower backwash flow rate will typically be required to achieve the same percent bed expansion as a conventional resin.

Figure 4 displays the backwash expansion characteristics of DOWEX MARATHON A2 resin in the hydroxide, chloride, and sulfate forms. The flow rate required to expand the resin bed to a given percentage above the settled volume can be estimated. An expansion of approximately 80% for a period of at least 20 minutes is normally suggested to achieve a flow rate capable of removing the particulate matter from the resin bed.

Figure 5 gives the backwash expansion flow rates for DOWEX MARATHON A2 resin as a function of temperature. The temperature of the water has a significant effect on the bed expansion during backwash. Hence, backwash flow rates may require adjustments to compensate for seasonal temperature changes. Failure to do so may result in either insufficient backwash or resin losses. For example, a backwash flow rate of 3.5 gpm/ft² will expand the resin bed, depending on the water temperature, as follows:

80% at 70°F
120% at 35°F

*Figure 4. Backwash Expansion vs. Flow Rate DOWEX MARATHON A2 Resin*

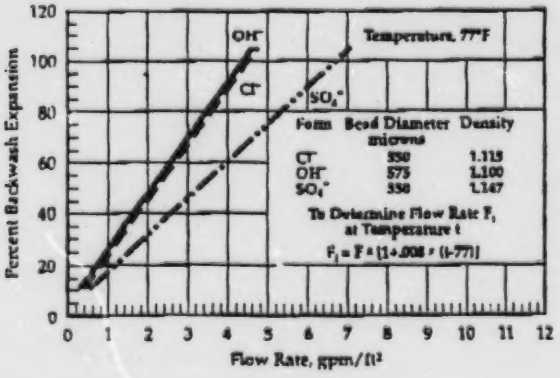
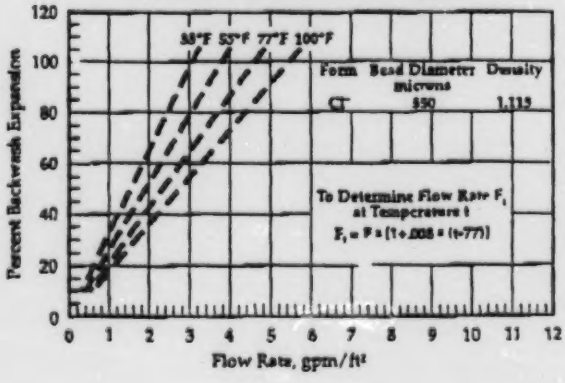



*Figure 5. Backwash Expansion vs. Flow Rate—Effect of Temperature DOWEX MARATHON A2 Resin*


Percent Backwash Expansion
Flow Rate, gpm/ft²
55°F 55°F 77°F 100°F
Form Bead Diameter microns Density
Cl⁻ 550 1.115
To Determine Flow Rate F₁ at Temperature t
F₁ = F × [1+.008 × (t-77)]

**For further information, call 1-800-447-4369**
**Ask for DOWEX® Ion Exchange Resins**

WARNING: Oxidizing agents such as nitric acid attack organic ion exchange resins under certain conditions and could result in slightly degraded resin or even an explosive reaction. Before using strong oxidizing agents, consult sources knowledgeable in handling such materials.

NOTICE: Dow believes the information and recommendations herein to be accurate and reliable as of June, 1991, to June, 1992, or when revised, whichever is earlier, and that Dow's products mentioned herein are reasonably fit for the recommended purposes. However, as use conditions are not within its control, Dow does not guarantee results from use of such products or other information contained herein. No warranty, express or implied, is given. As government regulations and use conditions may change, it is the Buyer's responsibility to determine the appropriateness of Dow's products for the Buyer's specific end uses and to comply with the law. Freedom from patents of Dow or others is not to be inferred.

Printed in U.S.A. ETHERIDGE8485I/REQ.490181 *Trademark of The Dow Chemical Company Form No. 177-1427-691 AMS

**TETRA Process Technologies** *TETRA Confidential* **Higgins Loop™ Pilot Test Run Summary**

| | | | |
|---|---|---|---|
| TETRA Project No: 22026 | Test No: 03 | | Page 1 |
| Process: Caustic Production from Brine & Lime | Date: 14-Jan-00 | | |
| Client: W. J. Wilson & Associates | Revision: 00 | File Name: | WJW03-J14.XLS |

**Objectives & Initial Conditions**

Set Service Cycle = 4.0 Min; Resin Pulse = 12"; Rinse, Wash & Displace = 600 Mls & 1.0 Min.
Lime - 110% of Stoich; NaCl - 110% of Stoich. NaCl Strength - 15% - Designed to Produce 9.8% NaOH
Reduce lime concentration to 2.6% and double flow rate to increase amount of soluble OH in regenerant solution

**Test Performance Summary: Separation Efficiencies, etc.**

| | | | | | |
|---|---|---|---|---|---|
| NaOH Product: | 3.48% NaOH | Specific Gravity: | 1.080 | Mass Balance Period: | 120 Minutes |
| | 3.94% Cl | | | Serv. Cycle Time: | 4.0 Minutes |
| Equivalent Cl: | 11.3% Cl in 10% NaOH | | | Total Run Period: | 255 Minutes |
| $Ca(OH)_2$ Feed: | 2.7% $Ca(OH)_2$ | Specific Gravity: | 1.020 | Resin Working Cap'y: | 31.2% of Theoretical |
| | 2.1% CaO | | | OH Regen'd Resin: | 0.451 Equ/L OH |
| | 2.2% Wt-% Solids | | | Cl-Loaded Resin: | 0.045 Equ/L OH |
| | | | | Resin Flow Rate: | 154.5 Mls/Min |

**MATERIAL BALANCE SUMMARY**

Mass Balance Period: *120* Minutes

| | Volume (L) | Spec Gravity | Weight (Kg) | Avg Flow (Ml/Min) | Hydroxide (N) | Hydroxide (Gms) | Chloride (N) | Chloride (Gms) | Sodium (GPL) | Sodium (Gms) | Calcium (N) | Calcium (Gms) | S. Solids (Wt-%) | S. Solids (Gms) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **Input Streams** | | | | | | | | | | | | | | |
| Lime Slurry Regen | 27.7 | 1.020 | 28.3 | 231 | 0.75 | 353.6 | - | | - | | 0.05 | 25.0 | 2.23 | 630.7 |
| Sodium Chloride Feed | 4.7 | 1.110 | 5.2 | 39 | | | 2.76 | 462.5 | - | | - | | - | |
| Pulse Water | | | | | | | | | | | | | | |
| Fresh Water Supply | 32.0 | 1.000 | 32.0 | 267 | | | | | | | | | | |
| Total Inputs: | 64.4 | | 65.5 | | Gms = | 353.6 | Gms = | 462.5 | Gms = | | Gms = | 25.0 | Gms = | 630.7 |
| **Output Streams** | | | | | | | | | | | | | | |
| Sodium Hydroxide | 7.5 | 1.080 | 8.1 | 63 | 0.94 | 119.9 | 1.20 | 319.5 | - | | - | | - | |
| Calcium Chloride | 46.0 | 1.010 | 46.5 | 383 | 0.28 | 219.0 | 0.21 | 342.9 | - | | 0.20 | 182.2 | 0.61 | 283.4 |
| Rinse Slip Water | | | | | | | | | - | | - | | - | |
| Displaced Water | 12.0 | 1.000 | 12.0 | 100 | 0.03 | 6.1 | 0.04 | 17.0 | - | | - | | - | |
| Backwash Water | | 1.000 | | | | | | | - | | - | | - | |
| Total Outputs: | 65.5 | | 66.6 | | Gms = | 344.9 | Gms = | 679.5 | Gms = | | Gms = | 182 | Gms = | 283 |
| Recovery: | | | 102% | | | 97.6% | | 146.9% | | #DIV/0! | | 729.9% | | 44.9% |

**RESIN DATA**

**Resin Type, Capacity & Flow Data**

| | | | | | |
|---|---|---|---|---|---|
| Resin Name: | *Dowex Marathon A2* | Resin Capacity = | *1.30* Equ/L | Service Cycle = | *4.0* Minutes |
| Type: | *Strong Base Anion* | Flow Rate = | 154.5 Mls/Min | Resin Pulse Length = | *12.0* Inches |
| Manufacturer: | *Dow Chemcial* | Resin Velocity = | 3.0 In/Min | Resin Vol Processed = | 18.5 Liters |

**Data Interpretation & Remarks**

No significant improvements in resin regeneration occurred with the diluted lime slurry. The resin's working capacity is still low (31%). Following the run, a meeting was held to discuss some of the differences between the prior work by W.J. Wilson and the TETRA pilot. The OH-regen'd resin was not analyzed in prior work, so this could not be compared. To fully regenerate the resin, Wilson "scrubbed" the regenerated resin with a portion of NaOH product, and NaOH strength was increased by adding product to the NaCl feed.

**TETRA Process Technologies** Date: 14-Jan-00 Run No: 03

Higgins Loop™ Pilot Test - Analytical Data

Project No. 22026

© - Routine Sample

| | Sample I.D. | Hydroxide "GU" or "GPLI" (N) | Chloride "GPLI" ONLY (N) | Sodium "GPLI" ONLY (GPL) | Calcium "GU" or "GPLI" (N) | S. Solids (Wt-%) | Specific Gravity (Gm/CC) |
|---|---|---|---|---|---|---|---|
| Analytical Method | | Base Titrate | $AgNO_3$ Titer | A.A. | EDTA Titer | Filtration | Mettler Bal |
| Molecular Weight | | 17.0 | 35.5 | 23.0 | 40.0 | | |
| Equivalent Weight | | 17.0 | 35.5 | 23.0 | 20.0 | | |
| **Terminal Samples** | | | | | | | |
| Feed Samples | | | | | | | |
| Lime Slurry Regen | A | © 0.750 | | | © 0.045 | © 2.23 | © 1.02 |
| Sodium Chloride Feed | B | © | © 2.760 | © | | | © 1.11 |
| Pulse Water | C | © | © | © | | | |
| Effluent Samples | | | | | | | |
| SET # 1 Sodium Hydroxide | D | © 0.940 | © 1.200 | S | S | | © 1.08 |
| SET # 1 Calcium Chloride | E | F | © 0.210 | S | © 0.198 | © 0.61 | © 1.01 |
| | | T 0.280 | | | | | |
| SET # 1 Rinse Slip Water | F | © | © | | | | © |
| SET # 1 Displaced Water | G | © 0.030 | © 0.040 | S | S | | © 1.00 |
| SET # 1 Backwash Water | H | © | © | | | S | © |
| SET # 2 Sodium Hydroxide | D | © | © | S | S | | © |
| SET # 2 Calcium Chloride | E | F | © | S | © | © | © |
| | | T | | | | | |
| SET # 2 Rinse Slip Water | F | © | © | | | | © |
| SET # 2 Displaced Water | G | © | © | S | S | | © |
| SET # 2 Backwash Water | H | © | © | | | © | S |
| **Resin Samples** | | | | | | | |
| Cl-Loaded Resin | J | © 0.045 | © 1.730 | | | | |
| OH-Regenerat'd Resin | K | © 0.451 | © 0.670 | | | | |
| **Loop Samples** | | | | | | | |
| Wash #1 | L | T | | | | © | S |
| Regeneration #1 | M | | © 0.060 | | | | S 1.03 |
| Regeneration #2 | N | | © 0.120 | | | | S 1.02 |
| Effluent #3 | O | | © | | | | S |
| Rinse #1 | P | | © 0.79 | | | | |
| Production #1 | R | © 0.265 | © 2.610 | | | | |
| Production #2 | S | © 0.330 | © 2.500 | | | | |
| Production #3 | T | © 0.540 | © 2.190 | | | | |
| Displacement | U | S | | | | | |
| Backwash | V | S | | | | | |

Analyses in N on Resin

Pass 125 Mls 2N KNO3 thru 25 Mls of resin. Rinse with DI $H_2O$. Collect 200 Mls effluent for assay (x 8).

© Routine S Special F Filtered T Total (sugar)

| Special Samples | Assay: | Hydroxide | Chloride | Sodium | Calcium | S. Solids | Sp Gravity |
|---|---|---|---|---|---|---|---|
| | | | | | | | |
| | | | | | | | |
| | | | | | | | |
| | | | | | | | |

**TETRA Process Technologies** *TETRA Confidential* **Higgins Loop™ Pilot Test Run Summary**

| | | | | | |
|---|---|---|---|---|---|
| TETRA Project No: | 22026 | Test No: | 04 | | Page 1 |
| Process: | Caustic Production from Brine & Lime | Date: | 15-Jan-00 | | |
| Client: | W. J. Wilson & Associates | Revision: | 00 | File Name: | WJW04-J15.XLS |

**Objectives & Initial Conditions**

Service Cycle, Resin Pulse, Rinse, Wash & Displace Flows, Feed Stoichiometries remain the same.
Spike 15% NaCl feed with 0.8% NaOH from Product to increase NaOH product strength. Add caustic to wash & pulse water to "scrub" regenerated resin.
Keep lime concentration at 2.6% and flow rate doubled to increase amount of soluble OH in regenerant solution

**Test Performance Summary: Separation Efficiencies, etc.**

| | | | | | | |
|---|---|---|---|---|---|---|
| NaOH Product: | 4.09% NaOH | Specific Gravity: | 1.100 | Mass Balance Period: | 90 | Minutes |
| | 5.71% Cl | Net Product Increase: | 3.33% NaOH | Serv. Cycle Time: | 4.0 | Minutes |
| Equivalent Cl: | 14.6% Cl in 10% NaOH | | | Total Run Period: | 255 | Minutes |
| $Ca(OH)_2$ Feed: | 2.8% $Ca(OH)_2$ | Specific Gravity: | 1.030 | Resin Working Cap'y: | 26.0% | of Theoretical |
| | 2.1% CaO | | | OH Regen'd Resin: | 0.450 | Equ/L OH |
| | 2.1% Wt-% Solids | | | Cl-Loaded Resin: | 0.112 | Equ/L OH |
| | | | | Resin Working Cap'y After Scrub: | 29.1% | or 3.1% Change |

**MATERIAL BALANCE SUMMARY**

Mass Balance Period: 90 Minutes

| | Volume (L) | Spec Gravity | Weight (Kg) | Avg Flow (Ml/Min) | Hydroxide (N) | Hydroxide (Gms) | Chloride (N) | Chloride (Gms) | Sodium (GPL) | Sodium (Gms) | Calcium (N) | Calcium (Gms) | S. Solids (Wt-%) | S. Solids (Gms) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **Input Streams** | | | | | | | | | | | | | | |
| Lime Slurry Regen | 22.4 | 1.030 | 23.1 | 249 | 0.77 | 293.5 | - | | - | | 0.05 | 22.4 | 2.08 | 480.3 |
| Sodium Chloride Feed | 6.5 | 1.110 | 6.5 | 66 | 0.21 | 21.1 | 3.18 | 666.1 | - | | - | | - | |
| Pulse Water | 14.0 | 1.000 | 14.0 | 155 | 0.08 | 19.0 | 0.02 | 9.9 | | | | | | |
| Fresh Water Supply | 10.0 | 1.000 | 10.0 | 111 | | | | | | | | | | |
| Total Inputs: | 52.3 | | 53.6 | | Gms = | 333.5 | Gms = | 676.0 | Gms = | | Gms = | 22.4 | Gms = | 480.3 |
| **Output Streams** | | | | | | | | | | | | | | |
| Sodium Hydroxide | 5.4 | 1.100 | 5.9 | 60 | 1.13 | 103.3 | 1.77 | 339.3 | - | | - | | - | |
| Calcium Chloride | 36.0 | 1.020 | 36.7 | 400 | 0.35 | 214.2 | 0.19 | 242.8 | - | | 0.18 | 129.6 | 0.96 | 352.5 |
| Rinse Slip Water | | | | | | | | | - | | - | | - | |
| Displaced Water | 10.0 | 1.010 | 10.1 | 111 | 0.21 | 35.7 | 0.14 | 49.7 | - | | - | | - | |
| Backwash Water | | 1.000 | | | 0.08 | | 0.03 | | - | | - | | - | |
| Total Outputs: | 51.4 | | 52.8 | | Gms = | 353.2 | Gms = | 631.8 | Gms = | | Gms = | 130 | Gms = | 353 |
| Recovery: | | | 98% | | | 105.9% | | 93.5% | | #DIV/0! | | 578.1% | | 73.4% |

**RESIN DATA**

**Resin Type, Capacity & Flow Data**

| | | | | | |
|---|---|---|---|---|---|
| Resin Name: | *Dowex Marathon A2* | Resin Capacity = | *1.30* Equ/L | Service Cycle = | *4.0* Minutes |
| Type: | *Strong Base Anion* | Flow Rate = | 154.5 Ml/Min | Resin Pulse Length = | *12.0* Inches |
| Manufacturer: | *Dow Chemcial* | Resin Velocity = | 3.0 In/Min | Resin Vol Processed = | 13.9 Liters |

**Data Interpretation & Remarks**

Resin scrubbing with dilute NaOH in the wash zone improved the resin working capacity by 3.1% (0.045 to 0.049 Equ/L). NaOH product strength increased to 4.1%, but after correcting for its feed strength, the concentration increase is 3.3%. Most notably, resin conversion to the Cl form in the production zone was reduced by 5% (0.07 Equ/L) due to the presence of NaOH in the feed. This affects the equilibrium between the resin & liquid phases, increasing the resin's OH concentration.

**TETRA Process Technologies** Date: 15-Jan-00 Run No: 04

Higgins Loop™ Pilot Test - Analytical Data

Project No. 22026

© - Routine Sample

| | Sample I.D. | Hydroxide "(N)" or "(GPL)" (N) | Chloride "(GPL)" ONLY (N) | Sodium "(GPL)" ONLY (GPL) | Calcium "(N)" or "(GPL)" (N) | S. Solids (Wt-%) | Specific Gravity (Gm/CC) |
|---|---|---|---|---|---|---|---|
| Analytical Method | | Base Titrate | $AgNO_3$ Titer | A.A. | EDTA Titer | Filtration | Mettler Bal |
| Molecular Weight | | 17.0 | 35.5 | 23.0 | 40.0 | | |
| Equivalent Weight | | 17.0 | 35.5 | 23.0 | 20.0 | | |
| **Terminal Samples** | | | | | | | |
| Feed Samples | | | | | | | |
| Lime Slurry Regen | A | © 0.770 | | | © 0.050 | © 2.08 | © 1.03 |
| Sodium Chloride Feed | B | © 0.210 | © 3.180 | © | | | © 1.11 |
| Pulse Water | C | © 0.080 | © 0.020 | © | | | © 1.00 |
| Effluent Samples | | | | | | | |
| S Sodium Hydroxide | D | © 1.125 | © 1.770 | S | S | | © 1.10 |
| E Calcium Chloride | E | F 0.140 | © 0.190 | S | © 0.180 | © 0.96 | © 1.02 |
| T | | T 0.350 | | | | | |
| Rinse Slip Water | F | © | © | | | | © |
| # Displaced Water | G | © 0.210 | © 0.140 | S | S | | © 1.01 |
| 1 Backwash Water | H | © 0.080 | © 0.030 | | | S | © 1.00 |
| S Sodium Hydroxide | D | © | © | S | S | | © |
| E Calcium Chloride | E | F | © | S | © | © | © |
| T | | T | | | | | |
| Rinse Slip Water | F | © | © | | | | © |
| # Displaced Water | G | © | © | S | S | | © |
| 2 Backwash Water | H | © | © | | | © | S |
| **Resin Samples** | | | | | | | |
| Cl-Loaded Resin | J | © 0.112 | © 1.250 | | | | |
| OH-Regenerat'd Resin | K | © 0.450 | © 0.840 | | | | |
| OH-Pulsed Resin | K | © 0.490 | © 0.720 | | | | |
| **Loop Samples** | | | | | | | |
| Wash #1 | L | T | | | | © | S |
| Regeneration #1 | M | | © 0.060 | | | | S 1.03 |
| Regeneration #2 | N | | © 0.120 | | | | S 1.02 |
| Effluent #3 | O | | © | | | | S |
| Rinse #1 | P | | © 0.79 | | | | |
| Production #1 | R | © 0.265 | © 2.610 | | | | |
| Production #2 | S | © 0.330 | © 2.500 | | | | |
| Production #3 | T | © 0.540 | © 2.190 | | | | |
| Displacement | U | S | | | | | |
| Backwash | V | S | | | | | |

Analyses in N on Resin

Pass 125 Mls 2N KNO3 thru 25 Mls of resin. Rinse with DI $H_2O$. Collect 200 Mls effluent for assay (x 8).

© Routine S Special F Filtered T Total (sugar)

| Special Samples | Assay: | Hydroxide | Chloride | Sodium | Calcium | S. Solids | Sp Gravity |
|---|---|---|---|---|---|---|---|
| NaOH Product 1245 | | 0.980 | 1.460 | | | | 1.09 |
| Pulse Water 1300 | | 0.060 | 0.020 | | | | |
| | | | | | | | |
| | | | | | | | |

**TETRA Process Technologies** *TETRA Confidential* **Higgins Loop™ Pilot Test Run Summary**

| | | | | | |
|---|---|---|---|---|---|
| TETRA Project No: | 22026 | Test No. | 05 | | Page 1 |
| Process: | Caustic Production from Brine & Lime | Date: | 16-Jan-00 | | |
| Client: | W. J. Wilson & Associates | Revision: | 00 | File Name: | WJW05-J16.XLS |

**Objectives & Initial Conditions:** Service Cycle, Resin Pulse, Rinse, Wash & Displace Flows, Feed Stoichiometries, Lime Concentration remain the same. Repeat the condictions of Test Run #04.

**Test Performance Summary: Separation Efficiencies, etc.**

| | | | | | | |
|---|---|---|---|---|---|---|
| NaOH Product: | 3.68% NaOH | Specific Gravity: | 1.110 | Mass Balance Period: | 90 | Minutes |
| | 6.17% Cl | Net Product Increase: | 2.59% NaOH | Serv. Cycle Time: | 4.0 | Minutes |
| Equivalent Cl: | 16.8% Cl in 10% NaOH | | | Total Run Period: | 255 | Minutes |
| $Ca(OH)_2$ Feed: | 2.2% $Ca(OH)_2$ | Specific Gravity: | 1.020 | Resin Working Cap'y: | 26.2% | of Theoretical |
| | 1.7% CaO | | | OH Regen'd Resin: | 0.510 | Equ/L OH |
| | 1.8% Wt-% Solids | | | Cl-Loaded Resin: | 0.170 | Equ/L OH |
| | | | | Resin Working Cap'y After Scrub: | 20.8% | -or 5.4% Change |

**MATERIAL BALANCE SUMMARY**

Mass Balance Period: 90 Minutes

| | Volume (L) | Spec Gravity | Weight (Kg) | Avg Flow (Ml/Min) | Hydroxide (N) | Hydroxide (Gms) | Chloride (N) | Chloride (Gms) | Sodium (GPL) | Sodium (Gms) | Calcium (N) | Calcium (Gms) | S. Solids (Wt-%) | S. Solids (Gms) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **Input Streams** | | | | | | | | | | | | | | |
| Lime Slurry Regen | 23.0 | 1.020 | 23.5 | 256 | 0.62 | 242.5 | - | | - | | 0.04 | 18.4 | 1.79 | 420.1 |
| Sodium Chloride Feed | 4.8 | 1.110 | 5.3 | 53 | 0.30 | 24.5 | 2.82 | 480.5 | - | | - | | - | |
| Pulse Water | 14.2 | 1.010 | 14.3 | 158 | 0.11 | 26.6 | 0.11 | 55.5 | | | | | | |
| Fresh Water Supply | 10.5 | 1.000 | 10.5 | 117 | | | | | | | | | | |
| Total Inputs: | 52.5 | | 53.6 | | Gms = | 293.6 | Gms = | 536.0 | Gms = | | Gms = | 18.4 | Gms = | 420.1 |
| **Output Streams** | | | | | | | | | | | | | | |
| Sodium Hydroxide | 4.7 | 1.110 | 5.2 | 52 | 1.02 | 61.5 | 1.93 | 322.0 | - | | - | | - | |
| Calcium Chloride | 38.0 | 1.010 | 38.4 | 422 | 0.14 | 90.4 | 0.19 | 256.3 | - | | 0.15 | 114.0 | 0.23 | 88.3 |
| Rinse Slip Water | | | | | | | | | - | | - | | - | |
| Displaced Water | 10.0 | 1.000 | 10.0 | 111 | 0.17 | 28.9 | 0.14 | 49.7 | - | | - | | - | |
| Backwash Water | | 1.000 | | | 0.10 | | 0.08 | | - | | - | | - | |
| Total Outputs: | 52.7 | | 53.6 | | Gms = | 200.8 | Gms = | 628.0 | Gms = | | Gms = | 114 | Gms = | 88 |
| Recovery: | | | 100% | | | 68.4% | | 117.2% | | #DIV/0! | | 619.3% | | 21.0% |

**RESIN DATA**

**Resin Type, Capacity & Flow Data**

| | | | | | |
|---|---|---|---|---|---|
| Resin Name: | *Dowex Marathon A2* | Resin Capacity = | *1.30* Equ/L | Service Cycle = | *4.0* Minutes |
| Type: | *Strong Base Anion* | Flow Rate = | 154.5 Mls/Min | Resin Pulse Length = | *12.0* Inches |
| Manufacturer: | *Dow Chemcial* | Resin Velocity = | 3.0 In/Min | Resin Vol Processed = | 13.9 Liters |

**Data Interpretation & Remarks:** Resin scrubbing with dilute NaOH in the wash zone had no impact on the resin working capacity (5.4% reduction). Resin conversion to the Cl form in the production zone was lower in this run. Some of this may be attributed to loss of NaCl feed for the final 20 minutes of the run (failed valve solenoid). There was no change in process performance when compared with Run #04.

**TETRA Process Technologies** Date: 16-Jan-00 Run No: 05

Higgins Loop™ Pilot Test - Analytical Data

Project No. 22026

© - Routine Sample

| | Sample I.D. | Hydroxide "(N)" or "(GPL)" (N) | Chloride "(GPL)" ONLY (N) | Sodium "(GPL)" ONLY (GPL) | Calcium "(N)" or "(GPL)" (N) | S. Solids (Wt-%) | Specific Gravity (Gm/CC) |
|---|---|---|---|---|---|---|---|
| Analytical Method | | Base Titrate | $AgNO_3$ Titer | A.A. | EDTA Titer | Filtration | Mettler Bal |
| Molecular Weight | | 17.0 | 35.5 | 23.0 | 40.0 | | |
| Equivalent Weight | | 17.0 | 35.5 | 23.0 | 20.0 | | |
| **Terminal Samples** | | | | | | | |
| Feed Samples | | | | | | | |
| Lime Slurry Regen | A | © 0.620 | | | © 0.040 | © 1.79 | © 1.02 |
| Sodium Chloride Feed | B | © 0.300 | © 2.820 | © | | | © 1.11 |
| Pulse Water | C | © 0.110 | © 0.110 | © | | | © 1.01 |
| Effluent Samples | | | | | | | |
| S Sodium Hydroxide | D | © 1.020 | © 1.930 | S | S | | © 1.11 |
| E Calcium Chloride | E | F 0.050 | © 0.190 | S | © 0.150 | © 0.23 | © 1.01 |
| T | | T 0.140 | | | | | |
| Rinse Slip Water | F | © | © | | | | © |
| # Displaced Water | G | © 0.170 | © 0.140 | S | S | | © 1.00 |
| 1 Backwash Water | H | © 0.100 | © 0.080 | | | S | © 1.01 |
| S Sodium Hydroxide | D | © | © | S | S | | © |
| E Calcium Chloride | E | F | © | S | © | © | © |
| T | | T | | | | | |
| Rinse Slip Water | F | © | © | | | | © |
| # Displaced Water | G | © | © | S | S | | © |
| 2 Backwash Water | H | © | © | | | © | S |
| **Resin Samples** | | | | | | | |
| Cl-Loaded Resin | J | © 0.170 | © 1.420 | | | | |
| OH-Regenerat'd Resin | K | © 0.510 | © 0.670 | | | | |
| OH-Pulsed Resin | K | © 0.440 | © 0.680 | | | | |
| **Loop Samples** | | | | | | | |
| Wash #1 | L | T | | | | © | S |
| Regeneration #1 | M | | © | | | | S |
| Regeneration #2 | N | | © | | | | S |
| Effluent #3 | O | | © | | | | S |
| Rinse #1 | P | | © | | | | |
| Production #1 | R | © | © | | | | |
| Production #2 | S | © | © | | | | |
| Production #3 | T | © | © | | | | |
| Displacement | U | S | | | | | |
| Backwash | V | S | | | | | |

Analyses in N on Resin

Pass 125 Mls 2N KNO3 thru 25 Mls of resin. Rinse with DI $H_2O$. Collect 200 Mls effluent for assay (x 8).

© Routine S Special F Filtered T Total (sugar)

| Special Samples | Assay: | Hydroxide | Chloride | Sodium | Calcium | S. Solids | Sp Gravity |
|---|---|---|---|---|---|---|---|
| | | | | | | | |
| | | | | | | | |
| | | | | | | | |
| | | | | | | | |

**TETRA Process Technologies**
**Caustic Soda from Lime & Brine**

**W. J. Wilson Caustic I-X Production Process**
**Capacity: 8,000 STPY NaOH**

| | Strength | Production /Usage | | Anhydrous Unit US$ | Revenues/Costs Annual US$ | Percent of Total |
|---|---|---|---|---|---|---|
| **Production** | | | | | | |
| Caustic Soda | 9.8% | 8,000.0 | Tons 100% | $350 | $2,800,000 | 100.0% |
| Calcium Chloride | 7.7% | 12,210.0 | Tons 100% | | | |
| Product Strength | 38.0% | $30 | /Ton Freight | $180 | $0 | 0.0% |
| Byproduct Production: | NO | | | | | |
| **Revenues** | | | | | $2,800,000 | |
| **Chemical Usages** | | | | | | |
| Hydrated Lime | 5.3% | 8,135.8 | Tons 100% | $76 | $615,678 | 29.6% |
| Sodium Chloride | 16.5% | 13,000.0 | Tons 100% | $30 | $390,000 | 18.7% |
| Process Water & Waste Water | | 74,660.1 | K Gals | $2 | $149,320 | 7.2% |
| Ion Exchange Resin | 15.0% | 225.0 | $Ft^3$ | $200 | $45,000 | 2.2% |
| Electrical Energy (100 HP) | | 626,640.0 | KWH | $0.06 | $37,598 | 1.8% |
| LP Steam - $CaCl_2$ Evaporation | | 69,847.7 | Tons | $10 | $0 | 0.0% |
| Maintenance | | 2.5% | of Capital Costs | | $122,750 | 5.9% |
| Labor - 1 Operator per Shift | | 8,760.0 | Hrs | $20 | $175,200 | 8.4% |
| **Subtotal - Direct Costs** | | | | | $1,535,547 | 73.7% |
| **Indirect Costs** | | | | | | |
| Depreciation | | 10.0 | Yrs | | $491,000 | 23.6% |
| General & Administration | | 2.0% | of Revenues | | $56,000 | 2.7% |
| **Total Operating Costs** | | | | | $2,082,547 | |
| **Gross Profit** | | | | | $717,453 | |
| Return on Investment | 14.6% | Payback: | 6.8 Yrs | | | |
| **Capital Costs** | | | | | | |
| Higgins Loop Model 4848 System | 2 | Loops | | | $1,700,000 | |
| Lime Slaker & Feed System | | | 1,900 | PPH Feed | $250,000 | |
| Sodium Chloride Lixivator/Feed | | | 1,900 | PPH Feed | $150,000 | |
| Calcium Chloride Lime Drum Filter | 2.0 | $GPM/Ft^2$ | 40 | $Ft^2$ | $80,000 | |
| Calcium Chloride Evaporator | 2 | Effects | 17,000 | | $0 | |
| Caustic Storage & Transfer | | | | | $60,000 | |
| Net Equipment Costs: | | | | | $2,240,000 | |
| Off-sites: Unloading, Loadout & Tie-ins | | | | | $130,000 | |
| Ion Exchange Resin | | 1,500.0 | $Ft^3$ | $200 | $300,000 | |
| Installed Cost | 2.0 | Equipment Multiplier | | | $4,910,000 | |

Revised: 18-Oct-99

**TETRA CONFIDENTIAL**

**TETRA Process Technologies**
**Caustic Soda from Lime & Brine**

**W. J. Wilson Caustic I-X Production Process**
**Capacity: 8,000 STPY NaOH**

| | Strength | Production /Usage | | Anhydrous Unit US$ | Revenues/Costs Annual US$ | Percent of Total |
|---|---|---|---|---|---|---|
| **Production** | | | | | | |
| Caustic Soda | 9.8% | 8,000.0 | Tons 100% | $350 | $2,800,000 | 60.5% |
| Calcium Chloride | 7.7% | 12,210.0 | Tons 100% | | | |
| Product Strength | 38.0% | $30 | /Ton Freight | $180 | $1,831,500 | 39.5% |
| Byproduct Production: | YES | | | | | |
| **Revenues** | | | | | **$4,631,500** | |
| **Chemical Usages** | | | | | | |
| Hydrated Lime | 5.3% | 8,135.8 | Tons 100% | $76 | $615,678 | 21.0% |
| Sodium Chloride | 16.5% | 13,000.0 | Tons 100% | $30 | $390,000 | 13.3% |
| Process Water & Waste Water | | 74,660.1 | K Gals | $2 | $149,320 | 5.1% |
| Ion Exchange Resin | 15.0% | 225.0 | $Ft^3$ | $200 | $45,000 | 1.5% |
| Electrical Energy (100 HP) | | 626,640.0 | KWH | $0.06 | $37,598 | 1.3% |
| LP Steam - $CaCl_2$ Evaporation | | 69,847.7 | Tons | $10 | $698,477 | 23.8% |
| Maintenance | | 2.5% | of Capital Costs | | $145,250 | 5.0% |
| Labor - 1 Operator per Shift | | 8,760.0 | Hrs | $20 | $175,200 | 6.0% |
| **Subtotal - Direct Costs** | | | | | **$2,256,524** | 77.0% |
| **Indirect Costs** | | | | | | |
| Depreciation | | 10.0 | Yrs | | $581,000 | 19.8% |
| General & Administration | | 2.0% | of Revenues | | $92,630 | 3.2% |
| **Total Operating Costs** | | | | | **$2,930,154** | |
| **Gross Profit** | | | | | **$1,701,348** | |
| Return on Investment | 29.3% | Payback: | 3.4 Yrs | | | |
| **Capital Costs** | | | | | | |
| Higgins Loop Model 4848 System | 2 | Loops | | | $1,700,000 | |
| Lime Slaker & Feed System | | | 1,900 | PPH Feed | $250,000 | |
| Sodium Chloride Lixivator/Feed | | | 1,900 | PPH Feed | $150,000 | |
| Calcium Chloride Lime Drum Filter | 2.0 | $GPM/Ft^2$ | 40 | $Ft^2$ | $80,000 | |
| Calcium Chloride Evaporator | 2 | Effects | 17,000 | | $450,000 | |
| Caustic Storage & Transfer | | | | | $60,000 | |
| Net Equipment Costs: | | | | | $2,690,000 | |
| Off-sites: Unloading, Loadout & Tie-ins | | | | | $130,000 | |
| Ion Exchange Resin | | 1,500.0 | $Ft^3$ | $200 | $300,000 | |
| Installed Cost | 2.0 | Equipment Multiplier | | | **$5,810,000** | |

Revised: 18-Oct-99

**TETRA CONFIDENTIAL**

**W.J. Wilson and Associates Ltd.**
Industrial/Chemical Consultants
55 Smythe St., Apt. 514
Saint John, NB
E2L 5A2

Fax: 1 (506) 468-2575
Res: 1 (506) 657-7185

APPENDIX 2

February 7, 2000

# The Manufacture of Caustic Alkali from Lime and Salt by Ion Exchange. Studies with Tetra Technologies Pilot Plant in Clinton, Tennessee

W.J. Wilson
President
W.J. Wilson and Associates

Abstract

A study of the manufacture of caustic soda from lime and salt using Higgins Loop Technology gave only 4% caustic, instead of 10%. Our earlier work on fixed bed gave a maximum of 14.5% caustic and on Higgins Loop Technology, in 1991, gave 8% caustic soda. The difference is due to the fact that we were using 4% slurries instead of 0.1N slurries. The examination on the experimental data show that appropriate modifications of the Higgins Loop system were not made and our representations with respect to revamping of the liquid flows in the system, and recycles, were not implemented. We have terminated the project early and have instituted a series of studies using fixed beds in our laboratory and we have done one study which shows the fixed bed system to be quite effective in getting the target level of 10% product level.

Table of Contents

1. Abstract
2. List of Figures and Acknowledgements P.1
3. Introduction P.2
4. Point by Point Discussion of Report. P.4
5. Test Program Discussion P.7
6. Conclusions P.8
7. References and Appendices P.10

## List of Figures

Figure 1 - Flowsheet, drawing 1300-004

Figure 2 - Flowsheet, drawing 1300-003

## Acknowledgements

Tetra Process Technologies
W.J. Wilson and Associates
LAPADCO Inc.
Dept. of Natural Resources (VAMP)

**W.J. Wilson and Associates Ltd.**
Industrial/Chemical Consultants
55 Smythe St., Apt. 514
Saint John, NB
E2L 5A2

Fax: 1 (506) 468-2575
Res: 1 (506) 657-7185

February 7, 2000

# Higgins Loop Pilot Test Report

## Caustic Production from Lime and Brine

Comments on the Pilot Test Report

## INTRODUCTION

The Tetra Report (Ref.1) on our studies in Clinton, Tennessee was received on Thursday, Feb. 3, 2000, and this report covers our comments on that work, which we were able to view and participate in during the time we were in Tennessee, from the 7th of January to the 19th of January, 2000.

I had visited Tampa, Florida for talks with Richard Dennis in September 1999 , with a view to setting up conditions where they might be interested in doing a test study for us. At that time they were made aware of previous work that had been done on this subject, the manufacture of caustic from lime and salt, by Lake Industries, a predecessor company, in a report issued September 1991. (Ref.2) This study, under the direction of I.R. Higgins (now deceased), was able to demonstrate that, using 0.1N calcium hydroxide, they were able to make 8% caustic solution from lime and salt using the Higgins Contactor, later referred to as the Higgins Loop Technology (HLT). There were some flaws in this technology which affected the capital and operating costs and these were later reviewed by W.J. Wilson and Associates. Primarily these were the high excess of lime which was required to reach the goal, but that lime would not entirely be lost to the system as it could be recovered by filtration, and certain details as to the estimated price of the input chemicals, which were later amended.

In a re-examination of the system, we did some fixed bed studies which radically improved the system, and this 1996 report was delivered to Mr. Dennis at this time. This work was also done on the basis of a 0.1N solution and achieved levels of caustic up to 14.5% concentration, primarily by eliminating fresh water additions to the system, except in making lime slurries, and recycling other solutions through the system in appropriate places. In addition the tails from the regeneration of the bed with salt were passed to the bed during the loading with hydroxide, subsequent to completing the treatment with lime. In addition this gave additional stripping of chloride from the resin and the solution so generated was used as the fluid to dissolve salt for the treatment of the column to make caustic soda. At that time we were also determining what particle size was suitable, in the case of lime, to treat the column without developing blockages due to the presence of the lime slurry in the mix. This work however was not followed through at that time, particularly as we had learned from Tetra that they were able to process up to 8% slurries of solids in the micron range. Our experiments showed that lime, on slaking, gave a suitable particle size for this purpose, as shown by scanning electron microscopy, provided the coarse material was screened out through a 325 mesh screen. It appears that from reading the report that Mr. Dennis erroneously assumed that we had done ion-exchange experiments with high solid slurries. This was not the case.

Our purpose in discussing these matters with Tetra was in the hope that they would modify the HLT in such a way as to achieve the kind of results we got on the fixed bed system, including flow modifications, recycles, and so on, to achieve our objective. Copies of our report were left with them to explore this possibility.

Subsequent to that time we received material balances for such a system using HLT, not however incorporating such matters as recycles and additional caustic stripping. It was only when we came to review the work in the pilot study that we came to the conclusion that these material balances and costs papers, appendix C in the report, <u>were only computer simulations</u> and not backed up by any experimental data. It seems to me that it is foolhardy in extreme, in hindsight, to use computer simulations without significant technical data and it is rather unfortunate that we used them in calculations to examine the potential of this approach as far as HLT is concerned.

It should however be noted that with the dilute lime slurry we have been very successful with fixed bed technology and partially successful with HLT, where Higgins demonstrated that he could make an 8% solution.

However we assumed that the data from Tetra, before we commenced work, was sound and accordingly, with collaboration with LAPADCO and VAMP we proceeded to initiate a definitive study. That study began on the 8th of January and concluded on the 18 of January, 2000, when it was obvious that severe problems had arisen which required further consideration of the situation and a re-evaluation of procedures being followed.

What follows is a point by point discussion of the report, which will be followed by the conclusions we have reached as to what might be done to develop a successful process.

Point by Point discussion of Report.

Executive Summary

P.1, Paragraph 1 - No comment.

P.1, Paragraph 2 - We see no proof of this statement and we have demonstrated in the lab that we can obtain high yields which were not obtained in the Higgins Loop. As to the need for redundant equipment we question the fact that the fixed bed would necessitate the use of redundant equipment.

P.1, Paragraph 3 - Key objectives.

1. no comment

2. "Generate a caustic product with minimum chloride contamination, <0.5% Cl, which would make it acceptable for use in the same process." and also in other end uses such as KOH, etc.

   The chloride level in the caustic solution would depend on the end use, i.e. used as a caustic extraction liquor in bleaching. The only case for minimum chloride levels is where caustic is used as makeup in the cooking chemicals. We would need to compare chlorides levels in the white liquor of Kraft mills with what we produce to see if it could be used. I believe that most of the chloride in the white liquor comes from the wood, so that a high chloride level in the liquor being evaporated would be undesirable. This requires further study.

3. The computer projection in Figure 1 assumes the CaCl2 levels as 7% and the purpose of the study was to see if 4% lime slurry could achieve this objective.

4. This resin utilization of 1.1equ/l would represent 91.6% utilization of the resin capacity. This has never been achieved in the Higgins Loop, which the best results was 77%, and our work preparatory to this study showed, that by using a caustic recycle, and minimum additions of water, on a fixed bed, that degree of utilization could be achieved, i.e. 91.6%.

P.1, Paragraph 4 - The Higgins 1991 system for 8% caustic soda required 8-#7248 units at 3750 MTPY/unit.

This earlier work used dilute lime and it appears that the 4% lime slurry is less efficient.

While we were in Clinton, Tenn., we realized we were having a problem with 4% lime slurry and initiated studies that we completed on our return and these studies were:

1. Effects of varying lime slurries on resin conversion.

| | | |
|---|---|---|
| 4% | slurry = | 12.0% conversion |
| 1% | slurry = | 25.4% conversion |
| 0.5% | slurry = | 31.4% conversion |
| 0.1% | slurry = | 47.1% conversion |

It should be noted that these were static experiments with the lime added to the resin slurry at 100% of the stoichiometric amount and stirred for 5 minutes, followed by immediate filtration and analysis of the filtrate.

2. This was using the 4% lime slurry and contacting the resin with subsequent amounts of fresh 4% lime slurry to see if any further conversion of the resin was achieved.

| | | |
|---|---|---|
| 1st addition of fresh lime | = | 13.0% conversion |
| 2nd addition of fresh lime | = | 3.85% conversion |
| 3rd addition of fresh lime | = | 1.54% conversion |
| 4th addition of fresh lime | = | 0.46% conversion |
| 5th addition of fresh lime | = | 0.46% conversion |

RESULT: 19.3% conversion of resin after 5 treatments.

Each test was filtered and the resin washed before the next treatment with fresh lime. These were also all static experiments with 5 minutes stirring times.

The resin, after 5 treatments with fresh lime, was then stirred, again for 5 minutes, in twice the stoichiometric amount of KOH to see what amount of chloride was kicked off the resin. This turned our to be 11.5%, and when added to the 19.3% from the fresh lime treatments, equals 30.8% conversion of the resin.

NOTE: These experiments were done as static experiments and there was no flow through a column of resin. We would expect the successive treatments in an ion-exchanging column would give better results on a given sample of resin taken from the column.

P.1, Paragraph 5 - This statement does not take into account any modifications that might be incorporated to increase the possible exchange of ions and it is premature to make this statement, as is the sentence about the outfall of resin regeneration in this process. And as we recommended at the time a drastic revision of the hydraulics and liquid flows would be required to achieve the kinds of values that we achieved on fixed bed systems. I simply do not believe that the CCIX is necessarily inferior to the fixed bed performance. It is just a matter of reorganizing the system to achieve this and can be done in part by eliminating the fresh water flows in the system. This was the case when in 1991 the test achieved 8% caustic soda without any recycle.

P.1, Paragraph 6 - No comment.

Page 3 - In regard to the remaining items, mainly 2,3,4,5,6, the key to obtaining a efficient process is process modification and innovation, and in the light of the fact that nothing very innovative in the way of process changes were implemented, I felt that the time had come to take ourselves back to the lab and examine what could be done on the fixed bed system on a larger scale, as well as continue our analyses on the chemical process.

If we went to more dilute solutions the CaCl2 content would be lowered and the cost of recovery of the CaCl2 would increase, however, I have in my records 2 flowsheets (Fig.1 & 2) by Lake Industries, the predecessor company to Tetra, which propose treatments of the CaCl2 effluent on the earlier system. Figure 1 produces a CaCl2 product at 19% from 0.07N and precipitated calcium carbonate as the secondary product. The waste product is a salt solution, which is a disadvantage.

The second system, Figure 2, makes precipitated calcium carbonate, 48T/day, CaCl2 as before 19%, with most of the effluent converted to deionized water.

This latter one is of considerable interest because we were talking of use in pulp mills where precipitated calcium carbonate would be of use and the deionized water would find many uses in the mill such as boiler feed water and pulp rinse water. The CaCl2 could, following the Tetra process, be evaporated to merchant grade, 38% CaCl2.

P. 14, Caustic Scrubbing.

This is an illustration of the scrubbing process, which in our opinion is what we have proposed all along, that we need a recycle stage and this has been shown to work in the fixed bed system. But unfortunately we failed to get across our concept and no attempt was made by Tetra to initiate a study involving scrubbing, which was unfortunate.

Test Program Discussion

When we review the results of the five runs one can come to the following conclusions.

Runs number 1, 2, and 3 are essentially identical, with only minor alterations, and all of these gave around 3% caustic soda, far below the target of 10%. Clearly it was evident from the start that a 4% lime slurry was not an effective reagent and I consider that the results from Run 1 should have triggered a discussion of how to overcome this problem, either by diluting the lime, as indicated in the early figures, or allowing the slurry sufficient time in the column for hydroxide ions to be generated from the solid lime. Our experiments have shown that it takes about two minutes to achieve saturation of lime in solution and I believe a 4 minute cycle is probably inadequate.

Runs number 4 and 5 used around 2% lime slurry at double the flow rate and this only accentuated the difficulties of generating fresh hydroxide from the solid, and is entirely counter productive. I don't know why he should have doubled the flow rate.

I found about midway through the study that it was very difficult to get a useful discussion of what was going on from Mr. Dennis, and finally had to become somewhat aggressive to get our point across. Unfortunately this was not completely effective as we were continually faced with a negative view from Mr. Dennis, who seems to be unwilling to entertain new ideas, despite the fact that we had achieved the objective with dilute lime both at Lake Industries and in our own lab with a fixed bed system. I must admit that previous work with this group had been much easier, but in those days I dealt with the late Irwin Higgins who was a great innovator.

His experiment on the resin regeneration efficiency was poorly planned and the results failed to confirm our findings in the fixed bed system, something that should have given him cause for reflection.

CONCLUSIONS: The conclusions that we have come to as a result of this study are:

1. There was far to little effort to develop an exchange of ideas and to make radical modifications to the system after such discussion.

2. Clearly the higher the lime content the less effective it is in removing the chloride from the resin. This led me to consider, but not implement, other possible sources of providing the source of hydroxide ion such as the use zinc-ammonium hydroxide, where the byproduct would be zinc chloride. These and other concepts will need to be thought through a little more completely in the future.

3. We need to review, experimentally, in a series of brief experiments a fixed bed system as an alternative to the HLT. In this we have already achieved a suitable product with dilute lime, and we will need to study the best situation relative to lime concentration and product concentration.

   If we had to revert to the 0.1N lime, I am attaching a system flowsheet (Fig. 2) for the treatment of such an effluent particularly where the preferred system would be one which generates precipitated calcium carbonate, 19% $CaCl_2$, and deionized water. All of which would be useful, with the first and third items being quite useful in a pulp mill.

Evaluation of the process in terms of cost recovery will be necessary to select the optimum conditions and configuration for the system.

4. If we continue with the HLT it must be obvious to all now that a drastic modification of the system flows will be necessary if we are to be successful, and I believe we should do a cost benefit study based on our lab work in New Brunswick, which is in progress on the fixed bed system, to evaluate the complete system as sketched in my 1996 report.

5. I still feel that we have the makings of a very useful process, but all parties involved in the experimental work need to be very innovative and we need to pursue this matter with vigour. This is one of the reasons I decided we were not making progress with Tetra and to pull out and use the funds to try the fixed bed approach.

References

1. Tetra Process Technologies Report, Caustic Production from Lime and Brine, Jan. 8 to 18, 2000.

2. I.R. Higgins, et.al., Caustic Production Pilot Test Report, Tetra Technologies Inc., 1991.

3. W.J. Wilson, Manufacture of Caustic Soda from Lime and Salt by Ion Exchange: A Reexamination of the System, 1996.

Appendices

1. Tetra Technologies Report on Caustic Production from Lime and Brine, 2000.

2. Caustic Production Pilot Test Report, 1991.

3. Manufacture of Caustic Soda from Lime and Salt by Ion Exchange: A Reexamination of the System, 1996.

**Figure 1 (in back pocket)**

8% NaOH floesheet conversion of waster $CaCl_2$ to NaCl by CCIX (Preliminary)

**Figure 2 (in back pocket)**

Water demineralization by modified desal CCIX from 8% NaOH flowsheet (Preliminary)

**W.J. Wilson and Associates Ltd.**
Industrial/Chemical Consultants
55 Smythe St., Apt. 514
Saint John, NB
E2L 5A2

Fax: 1 (506) 468-2575
Res: 1 (506) 657-7185

APPENDIX 3

February 18, 2000

Development of a Caustic Process Using Fixed Bed Ion Exchanging.

W.J. Wilson
President
W. J. Wilson & Associates Ltd.

ABSTRACT

A study on the effect of different levels of lime slurry on the overall process of ion-exchanging while maintaining inputs constant for the other solutions. Three resin columns, each containing equal amounts of resin, were treated with three different levels of lime slurry, 4%, 2%, 0.5% to observe their effectiveness of removing chloride from the resin. Each was then treated with KOH to further strip the remaining chloride from the column and then treated with a KCL/KOH mixture to strip the product (KOH) from the resin.

The results made us realise that it was the rate at which the lime dissolved when it is depleted in the system due to ion-exchange that was the problem, and we did an experiment which showed us that it takes about 1.5 minutes for lime to reach saturation in water, and therefore the problem really lay in the rate of dissolution of the lime and the whole process was solubility rate controlled. Thus the concentration of the lime slurry is less important than the time factor in the utilization of the resin.

Proposals to study this effect have been planned.

Table of Contents


| | | Page |
|---|---|---|
| 1. | Abstract | |
| 2. | Introduction | 1 |
| 3. | Objectives | 1 |
| 4. | Experimental | 2 |
| 5. | Results | 3 |
| 6. | Discussion | 9 |
| 7. | Recommendations | 10 |
| 8. | Conclusions | 10 |
| 9. | Future Work | 10 |
| 10. | References | 11 |

| Tables | | Page |
|---|---|---|
| 1. | Table 1 | 3 |
| 2. | Table 2 | 4 |
| 3. | Table 3 | 5 |
| 4. | Table 4 | 7 |
| 5. | Table 5 | 8 |


Acknowledgements
W.J. Wilson and Assoc.
LAPADCO Inc.
Dept. of Natural Resources (VAMP)

## INTRODUCTION

The CCIX study at TETRA Technologies in Clinton, Tennessee failed to achieve any better than around 4% caustic in the product, in spite of the fact that previous studies in 1991, also at TETRA Technologies achieved 8% caustic soda, while studies done after 1991 in our lab gave us up to 14% caustic soda, using fixed bed techniques.

Attempts by TETRA to improve the 4% yield were unsuccessful, and our attempts to convince them that a major restructuring of the CCIX system, in terms of flows, recycles, etc., failed to convince them to adopt an innovative approach to solving this problem. Accordingly we felt we were not making progress there, in contrast to our previous experiences with studies on the CCIX system (Higgins Loop), and we decided to terminate the work in Tennessee.

On our return we began work on fixed bed systems along the same lines as done earlier in a report dated Feb. 29, 1996, titled "The Manufacture of Caustic Soda from Lime and Salt by Ion Exchange: A Reexamination of the System". This work gave high levels of caustic in the product and had the following sequences.

1. With the column in the chloride form we treated it with a lime suspension, in this case 0.1%.

2 Lime suspension was followed by a caustic solution to complete the stripping of the column as far as possible. This caustic solution was the tails from a previous run, which still contained useful caustic but was too dilute to be included in the product.

3. This was then followed by the salt solution made up in the effluent from the caustic addition after the loading with lime.

4. This led to the first stage of the next run with addition of lime.

We had a three column system already available, containing 6.6L of resin each in a 3 inch diameter column, which would give us adequate data for scale up to plant size.

## OBJECTIVES

The objectives of this work was to determine the effect of different levels of lime slurry on the overall process while maintaining inputs constant for the other solutions, and it is these experiments, described below, from which we can draw our conclusions, and also to confirm what we had already realised, that the level of lime slurry had a major effect in the exchange process and the exchange was inversely proportional to the strength of the lime slurry.

EXPERIMENTAL

We had three identical columns, as described above, and each was run separately. All flows were upflow and the effluents were taken in fractions and analysed for chloride and hydroxide. These results are tabulated in the attached tables and illustrated in the attached graphs.

The flow rate through the columns was constant at 90 ml/min throughout and fractions were taken at suitable intervals depending on the material emerging from the column. The concentration of the solutions used were as follows.

| Experiment | Solution | Volume | KCl grams/L | KOH grams/L |
|---|---|---|---|---|
| 1 | **4% Lime** | 8 litres | --- | --- |
| 1 | Resin Strip | 10 litres | --- | 134.10 |
| 1 | Product Strip | 8 litres | 226.04 | 92.02 |
| 2 | **2% Lime** | 16 litres | --- | --- |
| 2 | Resin Strip | 12 litres | --- | 134.10 |
| 2 | Product Strip | 8 litres | 226.04 | 92.02 |
| 3 | **0.5% Lime** | 60 litres | --- | --- |
| 3 | Resin Strip | 10 litres | --- | 134.10 |
| 3 | Product Strip | 8 litres | 226.04 | 92.02 |
| 4 | **0.1% Lime** | 128 litres | --- | --- |
| 4 | Resin Strip | 20 litres | --- | 130.74 |
| 4 | Product Strip | 20 litres | 190.23 | 87.53 |

These experiments were all done in the potassium system, making potassium hydroxide. The reason for this was the fact that the most likely first system to be built would be a potassium hydroxide system to supply Havelock Lime with the KOH needed to manufacture potassium sulphate from gypsum.

TABLE 1

RESULTS: The results obtained are given in the following tables.

Experiment no. 1 4% Lime Slurry

Lime addition

| Sample size | Chloride g/sample | Chloride g/litre | accumulated %Cl stripped from resin | Hydroxide g/sample | Hydroxide g/litre |
|---|---|---|---|---|---|
| 2L | 0.7 | 0.4 | 0.2 | 0.0 | 0.0 |
| 2L | 5.7 | 2.8 | 2.1 | 1.0 | 0.5 |
| 2L | 4.6 | 2.3 | 3.6 | 1.7 | 0.9 |
| 2L | 7.1 | 3.6 | 5.9 | 1.4 | 0.7 |
| 2L | 9.2 | 4.6 | 8.9 | 1.4 | 0.7 |
| 2L | 11.7 | 5.9 | 12.8 | 1.4 | 0.7 |
| Resin Strip | | | | expressed as KOH | |
| 2L | 47.2 | 23.6 | 28.3 | 21.3 | 10.7 |
| 2L | 87.9 | 43.9 | 57.2 | 70.7 | 35.4 |
| 2L | 7.8 | 3.9 | 59.8 | 203.1 | 101.6 |
| 1L | 6.4 | 6.4 | 61.9 | 118.9 | 118.9 |
| 1L | 6.4 | 6.4 | 64.0 | 126.8 | 126.8 |
| 0.5L | 3.9 | 7.8 | 65.3 | 62.8 | 125.7 |
| 0.5L | 3.9 | 7.8 | 66.6 | 60.9 | 121.8 |
| 0.5L | 3.2 | 6.4 | 67.6 | 61.2 | 122.3 |
| 0.5L | 3.2 | 6.4 | 68.6 | 60.6 | 121.2 |
| Product Strip | | | | expressed as KOH | |
| 0.5L | 3.2 | 6.4 | --- | 62.8 | 125.7 |
| 0.5L | 2.8 | 5.7 | --- | 64.8 | 129.6 |
| 0.5L | 3.2 | 6.4 | --- | 73.5 | 147.0 |
| 0.5L | 11.3 | 22.6 | --- | 87.5 | 175.1 |
| 0.5L | 11.0 | 22.0 | --- | 86.4 | 172.8 |
| 0.5L | 23.8 | 47.5 | --- | 74.4 | 148.7 |
| 1L | 86.5 | 86.5 | --- | 56.1 | 112.2 |

TABLE 2

Experiment no. 2 2% Lime Slurry

Lime addition

| Sample size | Chloride g/sample | Chloride g/litre | accumulated %Cl stripped from resin | Hydroxide g/sample | Hydroxide g/litre |
|---|---|---|---|---|---|
| 2L | 1.4 | 0.7 | 0.5 | 0.0 | 0.0 |
| 2L | 7.8 | 3.9 | 3.0 | 0.7 | 0.4 |
| 2L | 14.9 | 7.4 | 7.9 | 1.0 | 0.5 |
| 2L | 14.2 | 7.1 | 12.6 | 1.0 | 0.5 |
| 2L | 13.1 | 6.6 | 16.9 | 1.0 | 0.5 |
| 2L | 12.8 | 6.4 | 21.1 | 1.0 | 0.5 |
| 2L | 12.8 | 6.4 | 25.3 | 1.0 | 0.5 |
| 2L | 12.1 | 6.0 | 29.3 | 1.0 | 0.5 |
| 2L | 9.2 | 4.6 | 32.1 | 1.4 | 0.7 |
| 2L | 7.8 | 3.9 | 34.9 | 1.4 | 0.7 |
| Resin Strip | | | | expressed as KOH | |
| 2L | 41.8 | 20.9 | 48.7 | 2.2 | 1.1 |
| 2L | 46.8 | 23.4 | 64.1 | 176.2 | 88.1 |
| 2L | 17.0 | 8.5 | 69.7 | 233.4 | 116.7 |
| 2L | 9.2 | 4.6 | 72.7 | 245.8 | 122.9 |
| 1L | 3.6 | 3.6 | 73.9 | 129.6 | 129.6 |
| 1L | 2.1 | 2.1 | 74.6 | 125.7 | 125.7 |
| 0.5L | 1.2 | 2.4 | 75.0 | 63.4 | 126.8 |
| 0.5L | 1.2 | 2.4 | 75.4 | 62.0 | 124.0 |
| 0.5L | 1.6 | 3.2 | 75.9 | 60.3 | 120.6 |
| 0.5L | 1.6 | 3.2 | 76.4 | 70.4 | 140.8 |
| Product Strip | | | | expressed as KOH | |
| 0.5L | 1.6 | 3.2 | --- | 85.9 | 171.7 |
| 0.5L | 1.6 | 3.2 | --- | 95.1 | 190.2 |
| 0.5L | 2.8 | 5.6 | --- | 94.6 | 189.1 |
| 0.5L | 29.2 | 58.5 | --- | 68.2 | 136.4 |
| 0.5L | 43.3 | 86.5 | --- | 49.9 | 99.9 |
| 0.5L | 43.6 | 87.2 | --- | 47.7 | 95.4 |
| 1L | 86.5 | 86.5 | --- | 96.5 | 96.5 |

TABLE 3

Experiment no. 3 0.5% Lime Slurry

Lime addition

| Sample size | Chloride g/sample | Chloride g/litre | accumulated %Cl stripped from resin | Hydroxide g/sample | Hydroxide g/litre |
|---|---|---|---|---|---|
| 2L | 1.4 | 0.7 | 0.5 | 0.00 | 0.00 |
| 2L | 2.1 | 1.1 | 1.2 | 0.06 | 0.03 |
| 2L | 5.0 | 2.5 | 2.8 | 0.03 | 0.02 |
| 2L | 5.0 | 2.5 | 4.4 | 0.03 | 0.02 |
| 2L | 5.0 | 2.5 | 6.0 | 0.03 | 0.02 |
| 2L | 4.2 | 2.1 | 7.5 | 0.06 | 0.03 |
| 2L | 4.2 | 2.1 | 8.8 | 0.03 | 0.02 |
| 2L | 5.6 | 2.8 | 10.7 | 0.13 | 0.06 |
| 2L | 5.6 | 2.8 | 12.6 | 0.30 | 0.15 |
| 2L | 7.1 | 3.5 | 14.9 | 0.70 | 0.35 |
| 2L | 5.6 | 2.8 | 16.8 | 0.30 | 0.15 |
| 2L | 5.0 | 2.5 | 18.4 | 0.30 | 0.15 |
| 2L | 4.3 | 2.1 | 19.8 | 0.30 | 0.15 |
| 2L | 4.3 | 2.1 | 21.2 | 0.30 | 0.15 |
| 2L | 4.3 | 2.1 | 22.6 | 0.30 | 0.15 |
| 2L | 4.3 | 2.1 | 24.0 | 0.30 | 0.15 |
| 2L | 4.3 | 2.1 | 25.4 | 0.70 | 0.35 |
| 2L | 4.3 | 2.1 | 26.8 | 1.00 | 0.50 |
| 2L | 4.3 | 2.1 | 28.2 | 1.00 | 0.50 |
| 2L | 3.6 | 1.8 | 29.4 | 0.70 | 0.35 |
| 2L | 2.8 | 1.4 | 30.3 | 0.70 | 0.35 |
| 2L | 2.8 | 1.4 | 31.2 | 0.70 | 0.35 |
| 2L | 2.8 | 1.4 | 32.2 | 0.70 | 0.35 |
| 2L | 3.6 | 1.8 | 33.3 | 1.00 | 0.50 |
| 2L | 3.6 | 1.8 | 34.5 | 0.70 | 0.35 |
| 2L | 3.6 | 1.8 | 35.7 | 1.00 | 0.50 |
| 2L | 2.8 | 1.4 | 36.6 | 1.00 | 0.50 |
| 2L | 2.8 | 1.4 | 37.5 | 1.00 | 0.50 |
| 2L | 2.8 | 1.4 | 38.5 | 1.00 | 0.50 |
| 2L | 2.8 | 1.4 | 39.5 | 1.00 | 0.50 |
| 2L | 3.6 | 1.8 | 40.6 | 1.40 | 0.70 |
| Resin Strip | | | | expressed as KOH | |
| 2L | 17.7 | 8.9 | 46.4 | 25.8 | 12.9 |
| 2L | 68.0 | 34.0 | 68.8 | 144.8 | 72.4 |
| 2L | 29.8 | 14.9 | 78.6 | 212.1 | 106.1 |
| 1L | 8.5 | 8.5 | 81.4 | 116.2 | 116.2 |
| 1L | 7.1 | 7.1 | 83.7 | 121.8 | 121.8 |
| 0.5L | 3.2 | 6.4 | 84.7 | 64.5 | 129.0 |
| 0.5L | 3.2 | 6.4 | 85.7 | 63.4 | 126.8 |
| 0.5L | 1.6 | 3.2 | 86.2 | 63.4 | 126.8 |
| 0.5L | 1.6 | 3.2 | 86.7 | 63.4 | 126.8 |

TABLE 3 con't

Experiment no. 3 0.5% Lime Slurry

| Sample size | Chloride g/sample | Chloride g/litre | accumulated %Cl stripped from resin | Hydroxide g/sample | Hydroxide g/litre |
|---|---|---|---|---|---|
| Product Strip | | | | expressed as KOH | |
| 0.5L | 1.6 | 3.2 | --- | 63.4 | 126.8 |
| 0.5L | 1.0 | 2.0 | --- | 66.8 | 133.6 |
| 0.5L | 1.0 | 2.0 | --- | 69.3 | 138.6 |
| 0.5L | 1.6 | 3.2 | --- | 81.9 | 163.8 |
| 0.5L | 1.6 | 3.2 | --- | 96.8 | 193.6 |
| 0.5L | 0.7 | 1.4 | --- | 96.5 | 193.0 |
| 1L | 56.4 | 56.4 | --- | 71.5 | 143.0 |

TABLE 4

Experiment no. 4 0.1% Lime Slurry

Lime addition

| Sample size | Chloride g/sample | Chloride g/litre | accumulated %Cl stripped from resin | Hydroxide g/sample | Hydroxide g/litre |
|---|---|---|---|---|---|
| 20L | 0.0 | 0.00 | 0.00 | 0.00 | 0.00 |
| 0.1L | 0.0 | 0.00 | 0.00 | 0.00 | 0.00 |
| 20L | 7.0 | 0.35 | 2.33 | 0.00 | 0.00 |
| 0.1L | 0.04 | 0.40 | 2.34 | 0.00 | 0.00 |
| 20L | 42.5 | 2.13 | 16.33 | 0.00 | 0.00 |
| 0.1L | 0.2 | 2.00 | 16.39 | 0.00 | 0.00 |
| 20L | 35.5 | 1.77 | 28.04 | 0.00 | 0.00 |
| 0.1L | 0.2 | 2.00 | 28.10 | 0.00 | 0.00 |
| 20L | 35.5 | 1.77 | 39.80 | 3.40 | 0.17 |
| 0.1L | 0.10 | 1.00 | 39.80 | 0.03 | 0.30 |
| 20L | 14.2 | 0.71 | 44.45 | 37.40 | 1.87 |
| 0.1L | 0.07 | 0.70 | 44.48 | 0.20 | 2.00 |
| 8L | 2.24 | 0.28 | 45.21 | 19.04 | 2.38 |
| 0.1L | 0.01 | 0.10 | 45.22 | 0.22 | 2.22 |
| 2L | 1.42 | 0.71 | 45.68 | 2.38 | 1.19 |
| 2L | 1.42 | 0.71 | 46.15 | 2.38 | 1.19 |
| Resin Strip | | | | expressed as KOH | |
| 2L | 15.6 | 7.8 | 51.28 | 77.4 | 38.7 |
| 2L | 18.4 | 9.2 | 57.34 | 193.0 | 96.5 |
| 2L | 14.8 | 7.4 | 62.23 | 233.4 | 116.7 |
| 2L | 10.6 | 5.3 | 65.73 | 240.2 | 120.1 |
| 2L | 8.5 | 4.3 | 68.52 | 248.0 | 124.0 |
| 2L | 6.4 | 3.2 | 70.62 | 249.1 | 124.6 |
| 2L | 5.0 | 2.5 | 72.25 | 266.0 | 133.0 |
| 2L | 3.6 | 1.8 | 73.42 | 272.7 | 136.4 |
| 2L | 3.6 | 1.8 | 74.59 | 259.2 | 129.6 |
| 2L | 2.1 | 1.1 | 75.29 | 258.1 | 129.1 |
| Product Strip | | | | expressed as KOH | |
| 2L | 2.1 | 1.1 | --- | 257.0 | 128.5 |
| 2L | 2.8 | 1.4 | --- | 254.7 | 127.3 |
| 2L | 3.6 | 1.8 | --- | 283.9 | 141.9 |
| 2L | 48.9 | 24.5 | --- | 252.5 | 126.3 |
| 2L | 110.6 | 55.3 | --- | 220.0 | 110.0 |
| 2L | 148.2 | 74.1 | --- | 180.8 | 90.4 |
| 2L | 163.8 | 81.9 | --- | 170.6 | 85.3 |
| 2L | 170.2 | 85.1 | --- | 162.7 | 81.4 |

TABLE 5

Percent Resin Utilization

| Slurry | Utilization with: Lime | KOH | Total Utilization |
|---|---|---|---|
| 4% | 12.8 | 55.8 | 68.6 |
| 2% | 34.8 | 41.5 | 76.3 |
| 0.5% | 40.5 | 46.3 | 86.8 |
| 0.1% | 46.2 | 29.1 | 75.3 |

DISCUSSION

Examination of the results given above enabled us to pinpoint the reason as to why a 4% slurry, apparently, gave poorer results than the 0.1% slurry. The results in the effluent from the lime addition showed that equilibrium had not been reached according to the value given for the last addition, since significant chloride was still in the effluent. We had always wondered why it was that the kind of results obtained as given in Table #5 showed that the more dilute the slurry was the more effective it seemed to be in stripping chloride from the resin, and this led us to conjecture as why this should be the case. No explanation had ever been forthcoming from Mr. Higgins as to why this was the case and yet it would be in our best interest to process high slurry loadings completely, where we would obtain a high concentration of calcium chloride in the effluent. Reference to Mellors treatise (Ref#1) showed that, contrary to expectations, the presence of calcium chloride actually enhances the solubility of lime.

These facts made us realise that it was the rate at which the lime dissolved when it is depleted in the system due to ion-exchange that was the problem, and we did an experiment which showed us that it takes about 1.5 minutes for lime to reach saturation in water, and therefore the problem really lay in the rate of dissolution of the lime and the whole process was solubility rate controlled. This explanation fitted the facts given in Table #5, particularly when you consider that when you process the same amount of lime in the column, at a fixed rate, the more dilute the solution the more lime is dissolved simply because it takes more time to process 80 litres of solution than 8 litres of solution, which is the case with the 4% slurry. Furthermore we know that the system had not come to equilibrium due the chloride levels at the end of the loading of the 4% slurry.

It is desirable to process the 4% material so that the effluent would contain 6 to 7% calcium chloride and the probability therefore is that if we recycled the effluent from the lime addition back through the column the lime uptake in the resin would be increased, and we will study this point in the next phase of our work. This is particularly useful where we know now that we will get increased solubility of the lime with the increasing amount of calcium chloride present in the solution. Of course counteracting that effect will be the more aggressive re-exchange of chloride for hydroxide, but this can only be determined by experiment.

RECOMMENDATIONS

1. We must determine the time involved to develop a maximum loading of the hydroxide on the resin as a function of time, and where the equilibrium lies, and these will be the first studies that will be done to upgrade the system.

2. We may repeat this process at lower and/or higher levels of lime to optimize the exchange and achieve a maximum level of calcium chloride in the effluent.

3. Following the determination of the best option for application of lime through the resin, we will then fine tune the rest of the system to have appropriate levels of caustic applied following the lime, and what the composition of the alkali metal chloride might be in the subsequent resin strip and product strip, being that a high level of alkali metal is required in the product with a minimum level of chloride.

CONCLUSIONS

I consider that we have made a significant finding in this work, and have effectively solved the problem of lime addition with concentration, and I am convinced that the simple effect of recycling high lime levels will solve that problem. There are some other alternatives but we will not discuss them at this time because I believe what we have concluded here is the simplest approach.

Future Work

There are other studies ongoing in this work and we hope to bring them to a conclusion within weeks, mainly:

a. Literature Survey
b. Market Survey
c. Cost Benefit Analysis

This latter will depend on the outcome of the present work, but we are confident that a solution has been found to the problem. We also have data from RHOM & HAAS based on the designing of fixed bed ion-exchangers.

Althought these matters do not strictly come under the perview of the VAMP program, we will issue to the Dept. of Natural Resources confidential releases as subsidiary reports so that the Department canbe fully informedof theprogress of thisproject.

References

1. Mellor, J.W., Comprehensive Treatise on Inorganic Chemistry, ca. 1920

**W.J. Wilson and Associates Ltd.**
Industrial/Chemical Consultants
55 Smythe St., Apt. 514
Saint John, NB
E2L 5A2

Fax: 1 (506) 468-2575
Res: 1 (506) 657-7185

APPENDIX 4

March 8, 2000

Development of the Proposed Process.

W.J. Wilson and Associates
W.J. Wilson, Pres.

# TABLE OF CONTENTS


| | | |
|---|---|---|
| 1. | Introduction | P.1 |
| 2. | Experimental | P.1 |
| 3. | Table 1 | P.2 |
| 4. | Table 2 | P.3 |
| 5. | Table 3 | P.4 |
| 6. | Steps of Process | P.5 |

## INTRODUCTION



The previous reports identified the problems in the process we are studying and indicated the probable solutions to those problems. In this section we are proceeding to layout the process that will be used in the future studies, as well as the experimental data which leads us to these conclusions. These data are additional to those already reported.

The Tetra work showed that at 4% and 2% slurries low levels of calcium chloride were obtained, but offered no explanations to why. Our experimental work now indicates the problems we had to solve and how they may be solved to arrive at an acceptable process. The problems were:

1. The inadequate exchange of lime for chloride at the 4% level and that this situation improved as the suspension became more dilute. This was shown in Appendix 3. Thus only 10% to 15% of the resin was being used in the exchange and this would not generate enough caustic to drive the process and get an acceptable level of product in the product strip.

2. We have two major problems which we think we are solving:

   a. To increase the utilization of the resin, and
   b. To obtain as high as possible levels of calcium chloride in the effluent.

These two possibilities are conflicting with one another, as the results will show.

There is no problem in getting a high concentration of product if the resin is being substantially utilized, but in order to increase the utilization of the resin we had to take and examine several alternatives. These will be discussed in reference to the tables.

## EXPERIMENTAL

Various experiments were run to establish which was the most effect way of stripping chloride from the resin, and the most effective concentration of slurry to use, taking into account the ultimate problem of recovering calcium chloride as a by-product. These data are presented in the following tables, which are self explanatory.

TABLE 1 Continuation of 2% and 4% experiments referred to below in Appendix 3.

2% Lime Slurry flowed through column.

| Sample | grams/litre calcium chloride |
|---|---|
| 2L | 1.10 |
| 2L | 6.10 |
| 2L | 11.58 |
| 2L | 11.11 |
| 2L | 10.33 |
| 2L | 10.02 |
| 2L | 10.02 |
| 2L | 9.39 |
| 2L | 7.20 |
| 2L | 6.10 |
| Totals 20L | 82.95 divided by 20L = 4.15 g/l |

Total utilization of resin = 34.9%

4% Lime slurry flowed through column.

| Sample | grams/litre calcium chloride |
|---|---|
| 2L | 0.63 |
| 2L | 4.38 |
| 2L | 3.60 |
| 2L | 5.63 |
| 2L | 7.20 |
| 2L | 9.23 |
| Totals 12L | 30.67 divided by 12L = 2.56 g/l |

Total utilization of resin = 12.8%

TABLE 2 Recirculation of a 4% slurry, to try and increase the amount of chloride taken off the resin.

| | Sample | grams/litre calcium chloride |
|---|---|---|
| Fresh Slurry | 0.5L | 8.88 |
| | 2L | 8.33 |
| | 2L | 3.89 |
| | 2L | 3.89 |
| | 2L | 5.55 |
| | 8.5L | 30.54 divided by 8.5L = 3.59 g/l |
| Second Pass | 2L | 6.11 |
| | 2L | 6.66 |
| | 2L | 8.33 |
| | 2L | 7.22 |
| | 8L | 28.32 divided by 8L = 3.54 g/l |
| Third Pass | 2L | 6.66 |
| | 2L | 8.33 |
| | 2L | 8.33 |
| | 2L | 6.11 |
| | 8L | 29.43 divided by 8L = 3.68 g/l |
| Fourth Pass | 2L | 7.22 |
| | 2L | 5.55 |
| | 2L | 5.55 |
| | 2L | 8.88 |
| | 8L | 27.20 divided by 8L = 3.40 g/l |

The recirculation of the 4% slurry does not appear to increase the yield.

TABLE 3 Static experiments at 4% and 8% slurries, using 1 litre of resin.

4% slurry - volume = 1100mls

| Time | grams/litre calcium chloride | utilization of resin |
|---|---|---|
| 0.5hr | 9.99 | 15.23% |
| 1hr | 10.55 | 16.08% |
| 2hr | 10.55 | 16.08% |
| 3hr | 11.10 | 16.92% |

8% slurry - volume = 555mls

| Time | grams/litre calcium chloride | utilization of resin |
|---|---|---|
| 0.5hr | 14.43 | 11.11% |
| 1hr | 14.43 | 11.11% |
| 2hr | 14.43 | 11.11% |
| 3hr | 14.43 | 11.11% |

8% slurry - volume based on void volume of resin = 430mls

| Time | grams/litre calcium chloride | utilization of resin |
|---|---|---|
| 0.5hr | 15.54 | 9.27% |
| 1hr | 16.40 | 9.59% |
| 2hr | 15.54 | 9.27% |
| 3hr | 15.54 | 9.27% |

8% slurry - repeat of above void volume based experiment.

| Time | grams/litre calcium chloride | utilization of resin |
|---|---|---|
| 0.5hr | 15.54 | 9.27% |
| 1hr | 15.54 | 9.27% |
| 2hr | 15.54 | 9.27% |
| 3hr | 15.54 | 9.27% |

The most efficient method of stripping the column, of those studied in this report and those reported in Appendix 3, was the 2% solution, where in a single pass 82.95 grams of calcium chloride was in the effluent, and this represents a concentration of 4.15g/l calcium chloride, in a volume of 20 litres. In the case of 4% slurry, 30.67 grams of calcium chloride was recovered at a concentration of 2.56g/l in a volume of 12 litres.

These results should be compared with our static experiments, done on a smaller scale using 1 litre of resin, where the slurry was added to the resin in the chloride form, and after mixing allowed to stand for varying times, this gave 6.68 grams of calcium chloride in the solution, in a volume of 0.43 litres, which is the void volume of 1 litre of resin, which equates to a concentration of 15.5 g/l, which if done in a column situation would be 15.5 g/l at 5 litres or 77.5 grams of calcium chloride in the solution, compared to 82.95 grams of calcium chloride in a volume of 24 litres in the 2% slurry.

Of these, clearly the most satisfactory result is the 8% slurry, where the calcium chloride is approximately equal to that of the 2% experiment in the column requiring 24 litres.

In any of these processes there is a considerable excess of lime and this needs to be recovered for reuse. This is a simple filtration, lime not being very soluble, with a small amount of wash water to remove any calcium chloride adhering to the lime.

The calcium chloride solution will need to be concentrated to the market level of 38%, but we have another possibility, because we find that the lime residue retained on the 60 mesh filter contains lime and calcium carbonate in addition to some minor impurities such as iron and silica. We will therefore examine closely this residue to see what potential calcium chloride it would contain if we were to acidify it with hydrochloric acid, and these experiments will be completed at an early date.

There after the process will follow in the following steps.

1. Treat the resin in the stationery mode with a volume of 8% lime slurry equivalent to the void volume in the column. Allow it to stand for 1 to 2 hours. The actual time to be determined by experiment.

2. Flush the unused lime from the column, without mixing, using water.

3. The effluent, first fractions, will contain the excess lime as well as the chloride stripped from the resin. The excess lime will be recovered by filtration and the chloride present as calcium chloride will be passed to calcium chloride recovery. Experiments show that this calcium chloride solution, with appropriate separation of the fractions, will be around 1.5% calcium chloride.

4. The effluent from the sodium chloride treatment, together with some suspended lime, will also be filtered and the clear solution passed for salt or potassium chloride makeup.

5. The sodium chloride as developed above, together with added sodium chloride, will then be passed through the column to generate sodium hydroxide, thus returning the resin to the chloride form ready for a further treatment with lime.

6. The lime, prior to use, will be treated with water to slake it and to produce calcium hydroxide. This calcium hydroxide will then be passed through a 60 mesh screen which will give an accept fraction which will pass easily through the column and a reject fraction which will later be treated with hydrochloric acid, or other suitable acid, to give a calcium salt plus acid insoluble, mainly being silica. If we use hydrochloric acid the calcium chloride thus produced will be blended with the calcium chloride produced in the cycle and then treated to bring it to a market concentration of 38% or better.

7. The calcium hydroxide filtered from the material recovered from the column in the first stage will be blended with more lime and recycled.

This outlines the process which we have developed, which overcomes the problem of reaction of lime with resin, and produces a high concentration of calcium chloride as a byproduct.

The experimental work on this concept and scheme will begin immediately, as we have in hand three columns, each 6 feet in length, and 3 inches in diameter, and adequate resin to pack these columns. The study will continue beyond the funding of the VAMP Project.

This is a novel approach to this problem, which is the outcome of the studies we have done since we returned from Tennessee and the Tetra establishment, and we are forecasting a system which essentially is a batch operation but may in the long term be adaptable to a drastically modified Higgins Loop system or other continuous ion-exchanging systems.

This is essentially the completion of the work for the Vamp Project, but we plan to continue, to achieve a fully operable plant. We will make sure the Department is kept fully up to date on the developments of this future work.

Yours very truly

W.J. Wilson